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*Volume 141, Numbers 1-6*

*November-December, 1961*

# PROCEEDINGS OF THE ACADEMY OF SCIENCES

OF THE USSR

(DOKLADY AKADEMII NAUK SSSR)

Chemistry Section

IN ENGLISH TRANSLATION



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# SOME NEW DERIVATIVES OF IMIDO ESTERS

Academician A. E. Arbuzov and V. E. Shishkin

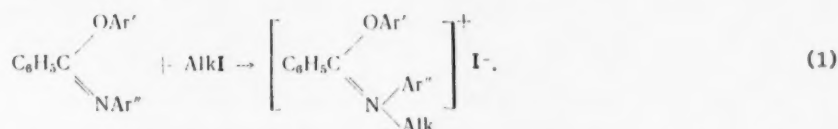
S. M. Kirov Kazan Chemical Technological Institute

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pp. 81-83, November, 1961

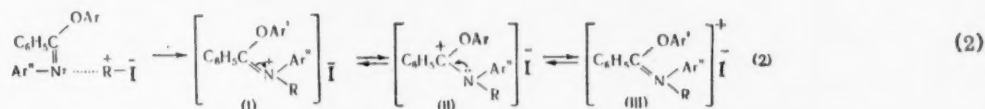
Original article submitted July 10, 1961

Alkyl imido esters react with alkyl halides with the formation of rearrangement products—amides of carboxylic acids [1-3]. We are the first to study the interaction of aryl imido esters with alkyl halides. It was found that the reaction with methyl iodide at 100° and with ethyl iodide at 130° takes place in only one direction with the formation of addition products. The reaction with benzimido esters substituted at the nitrogen atom, which we used in the present work, may be represented as follows:

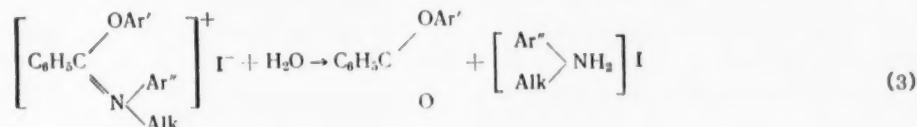


The addition products shown in Table 1 are new, previously unknown derivatives of imido esters. They may be named as alkiodides of imido esters. We assign an ionic salt structure to these alkiodides.

The reaction apparently begins with an electrophilic attack at the nitrogen atom with the formation of an immonium ion, which, together with the iodide anion, forms a salt (I). An electronic shift in the molecule is then possible with the formation of structures (II) and (III):

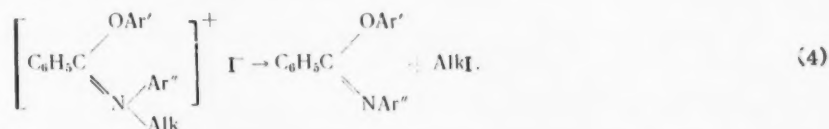


The ionic state of the iodine in the addition products and also that the alkyl group R (2) is bonded to the nitrogen atom was confirmed by hydrolysis. Even at ordinary temperatures, an acid reaction to litmus is obtained when the alkiodide is placed in water. Upon warming, hydrolysis takes place with the formation of aryl benzoates and alkylarylamines (3):



This method may be useful for the preparation of alkylarylamines.

At temperatures of 200-220°, decomposition of the alkiodides in which the alkyl halide is split off (4) takes place similarly to the decomposition of substituted ammonium salts:



Experiments on the synthesis of products of the addition of alkyl halides to the o-nitrophenyl and p- and o-chlorophenyl esters of N-phenylbenzimidic acid to N-p-chlorophenylbenzimidic acid phenyl ester were not successful.



Electronegative substituents apparently strongly repulse the free pair of electrons of the nitrogen atom through inductive and conjugation effects, and this suppresses the basic properties of the molecule. Confirmation of this point of view is to be found in reference [4], in which it is reported that N-phenylbenzimidic acid *o*-nitrophenyl ester does not form a salt with sulfuric acid. All of these addition products may be stored for prolonged periods in the absence of moisture (better under vacuum).

The N-*p*-ethoxyphenylbenzimidic acid phenyl ester and the N-*β*-naphthylbenzimidic acid phenyl ester used in this work were synthesized for the first time.

TABLE 1. Products of the Addition of Alkyl Halides to Imido Esters (product yields in all cases were close to theoretical)

Formula of compound $\left[ \begin{array}{c} \text{C}_6\text{H}_5\text{C} \begin{array}{l} \nearrow \text{OR}_1 \\ \searrow \text{N} \end{array} \begin{array}{l} \nearrow \text{R}_2 \\ \searrow \text{R}_3 \end{array} \end{array} \right]^+ \text{I}^-$	M.p. (dec.), °C	Crystal form	Empirical formula	I %	
				found	calc.
$\text{R}_1=\text{C}_6\text{H}_5$ ; $\text{R}_2=\text{C}_6\text{H}_5$ ; $\text{R}_3=\text{CH}_3$	160	Light yellow needles	$\text{C}_{20}\text{H}_{15}\text{NOI}$	30,52	30,55
$\text{R}_1=\text{C}_6\text{H}_5$ ; $\text{R}_2=\text{C}_6\text{H}_5$ ; $\text{R}_3=\text{C}_6\text{H}_5$	169	Same	$\text{C}_{21}\text{H}_{16}\text{NOI}$	29,78	29,56
$\text{R}_1=\text{C}_6\text{H}_5$ ; $\text{R}_2=\text{C}_6\text{H}_4\text{CH}_3\text{-o}$ ; $\text{R}_3=\text{CH}_3$	139—140	» »	$\text{C}_{21}\text{H}_{16}\text{NOI}$	29,63	29,56
$\text{R}_1=\text{C}_6\text{H}_5$ ; $\text{R}_2=\text{C}_6\text{H}_4\text{CH}_3\text{-o}$ ; $\text{R}_3=\text{C}_2\text{H}_5$	131—132	» »	$\text{C}_{22}\text{H}_{18}\text{NOI}$	28,74	28,62
$\text{R}_1=\text{C}_6\text{H}_5$ ; $\text{R}_2=\text{C}_6\text{H}_4\text{CH}_3\text{-p}$ ; $\text{R}_3=\text{CH}_3$	184	» »	$\text{C}_{21}\text{H}_{16}\text{NOI}$	29,70	29,56
$\text{R}_1=\text{C}_6\text{H}_5$ ; $\text{R}_2=\text{C}_6\text{H}_4\text{CH}_3\text{-p}$ ; $\text{R}_3=\text{C}_2\text{H}_5$	171—172	» »	$\text{C}_{22}\text{H}_{18}\text{NOI}$	28,62	28,62
$\text{R}_1=\text{C}_6\text{H}_5$ ; $\text{R}_2=\text{C}_{10}\text{H}_7\text{-β}$ ; $\text{R}_3=\text{CH}_3$	126—127	Light yellow prisms	$\text{C}_{24}\text{H}_{20}\text{NOI}$	27,11	27,27
$\text{R}_1=\text{C}_6\text{H}_5$ ; $\text{R}_2=\text{C}_{10}\text{H}_7\text{-β}$ ; $\text{R}_3=\text{C}_2\text{H}_5$	116—118	Same	$\text{C}_{25}\text{H}_{22}\text{NOI}$	26,42	26,47
$\text{R}_1=\text{C}_6\text{H}_5$ ; $\text{R}_2=\text{C}_6\text{H}_4\text{OCH}_3\text{-p}$ ; $\text{R}_3=\text{CH}_3$	175—176	» »	$\text{C}_{21}\text{H}_{16}\text{NO}_2\text{I}$	28,53	28,52
$\text{R}_1=\text{C}_6\text{H}_5$ ; $\text{R}_2=\text{C}_6\text{H}_4\text{OCH}_3\text{-p}$ ; $\text{R}_3=\text{C}_2\text{H}_5$	148—150	» »	$\text{C}_{22}\text{H}_{18}\text{NO}_2\text{I}$	27,60	27,63
$\text{R}_1=\text{C}_6\text{H}_5$ ; $\text{R}_2=\text{C}_6\text{H}_4\text{OC}_2\text{H}_5\text{-p}$ ; $\text{R}_3=\text{CH}_3$	179—180	» »	$\text{C}_{22}\text{H}_{18}\text{NO}_2\text{I}$	27,42	27,63
$\text{R}_1=\text{C}_6\text{H}_4\text{CH}_3\text{-o}$ ; $\text{R}_2=\text{C}_6\text{H}_5$ ; $\text{R}_3=\text{CH}_3$	181	Light yellow needles	$\text{C}_{21}\text{H}_{16}\text{NOI}$	29,93	29,56
$\text{R}_1=\text{C}_6\text{H}_4\text{CH}_3\text{-o}$ ; $\text{R}_2=\text{C}_6\text{H}_5$ ; $\text{R}_3=\text{C}_2\text{H}_5$	163—164	Same	$\text{C}_{22}\text{H}_{18}\text{NOI}$	29,00	28,62
$\text{R}_1=\text{C}_6\text{H}_4\text{CH}_3\text{-m}$ ; $\text{R}_2=\text{C}_6\text{H}_5$ ; $\text{R}_3=\text{CH}_3$	189—190	» »	$\text{C}_{21}\text{H}_{16}\text{NOI}$	29,41	29,56
$\text{R}_1=\text{C}_6\text{H}_4\text{CH}_3\text{-m}$ ; $\text{R}_2=\text{C}_6\text{H}_5$ ; $\text{R}_3=\text{C}_2\text{H}_5$	180—181	» »	$\text{C}_{22}\text{H}_{18}\text{NOI}$	28,58	28,62
$\text{R}_1=\text{C}_6\text{H}_4\text{CH}_3\text{-p}$ ; $\text{R}_2=\text{C}_6\text{H}_5$ ; $\text{R}_3=\text{CH}_3$	191	» »	$\text{C}_{21}\text{H}_{16}\text{NOI}$	29,65	29,56
$\text{R}_1=\text{C}_6\text{H}_4\text{CH}_3\text{-p}$ ; $\text{R}_2=\text{C}_6\text{H}_5$ ; $\text{R}_3=\text{C}_2\text{H}_5$	169—171	» »	$\text{C}_{22}\text{H}_{18}\text{NOI}$	28,35	28,62
$\text{R}_1=\text{C}_{10}\text{H}_7\text{-α}$ ; $\text{R}_2=\text{C}_6\text{H}_5$ ; $\text{R}_3=\text{CH}_3$	136—137	» »	$\text{C}_{24}\text{H}_{20}\text{NOI}$	27,01	27,27
$\text{R}_1=\text{C}_{10}\text{H}_7\text{-α}$ ; $\text{R}_2=\text{C}_6\text{H}_5$ ; $\text{R}_3=\text{C}_2\text{H}_5$	132	» »	$\text{C}_{25}\text{H}_{22}\text{NOI}$	26,81	26,47
$\text{R}_1=\text{C}_{10}\text{H}_7\text{-β}$ ; $\text{R}_2=\text{C}_6\text{H}_5$ ; $\text{R}_3=\text{CH}_3$	192—193	» »	$\text{C}_{24}\text{H}_{20}\text{NOI}$	27,13	27,27
$\text{R}_1=\text{C}_{10}\text{H}_7\text{-β}$ ; $\text{R}_2=\text{C}_6\text{H}_5$ ; $\text{R}_3=\text{C}_2\text{H}_5$	171	» »	$\text{C}_{25}\text{H}_{22}\text{NOI}$	26,41	26,47
$\text{R}_1=\text{C}_6\text{H}_4\text{CH}_3\text{-p}$ ; $\text{R}_2=\text{C}_6\text{H}_4\text{CH}_3\text{-p}$ ; $\text{R}_3=\text{CH}_3$	174—175	» »	$\text{C}_{22}\text{H}_{18}\text{NOI}$	28,58	28,62
$\text{R}_1=\text{C}_6\text{H}_4\text{CH}_3\text{-p}$ ; $\text{R}_2=\text{C}_6\text{H}_4\text{CH}_3\text{-p}$ ; $\text{R}_3=\text{C}_2\text{H}_5$	141	Light yellow prisms	$\text{C}_{23}\text{H}_{24}\text{NOI}$	27,47	27,74

#### EXPERIMENTAL

N-*p*-ethoxyphenylbenzimidic acid phenyl ester. a) On the basis of the work reported in references [5,6], N-*p*-ethoxyphenylbenzimidoyl chloride was prepared from 50 g of the *p*-phenetide and 43 g of phosphorus pentachloride by heating the mixture on a water bath. The phosphoryl chloride was distilled, and the reaction product was dissolved in 400 ml of dry ether and used for the synthesis of the imido ester. b) Sodium phenolate was prepared from 19,6 g of phenol and 4,8 g of sodium in a medium of 250 ml of anhydrous alcohol; the reaction was carried out in a flask fitted with a stirrer. The imidoyl chloride prepared in a) was added dropwise to the phenolate. The reaction mixture was filtered, and the precipitate was washed on the filter with water to remove the sodium chloride. Two recrystallizations from ethyl alcohol yielded 47 g (72%) of the imido ester as white plates with an m.p. of 112–113°. Found %: 4.51; 4.47.  $\text{C}_{21}\text{H}_{15}\text{NO}$ . Calculated %: 4.41.

The N-*β*-naphthylbenzimidic acid phenyl ester was prepared in a manner similar to that described above. The light yellow prismatic crystals (from alcohol) of imido ester melted at 101–102°; the yield was 68%. Found %: 4.37; 4.41.  $\text{C}_{23}\text{H}_{17}\text{NO}$ . Calculated %: 4.33.

Methiodide of N-phenylbenzimidic acid phenyl ester. A mixture of 20 g of N-phenylbenzimidic acid phenyl ester and 20 g of methyl iodide was sealed in a glass tube. The tube was held at 100° for 8 hours and was then opened. The contents were transferred to a casserole and the volatile material was evaporated under vacuum. The yellow

powder was recrystallized from a mixture of chloroform and ether. There was obtained 30 g (99%) of the methiodide of N-phenylbenzimidic acid phenyl ester with an m.p. of 160° (with decomposition). Found %: C 57.98; 57.77; H 4.40; 4.42; N 3.51; 3.57; I 30.52; 30.61.  $C_{20}H_{18}NOI$ . Calculated %: C 57.84; H 4.36; N 3.37; I 30.55.

Ethiodide of N-phenylbenzimidic acid phenyl ester was prepared in a manner similar to that described above from the imido ester and ethyl iodide; the reaction was carried out for 10 hours at 130°. The yield was 97%. M.p. 169° (with decomposition). Found %: C 58.58; 58.73; H 4.92; 4.67; N 3.41; 3.31; I 29.78; 29.81.  $C_{21}H_{20}NOI$ . Calculated %: C 58.75; H 4.68; N 3.26; I 29.56.

We used this method to synthesize a series of previously unknown derivatives of imido esters—products of the addition of alkyl iodides. Some of their properties were studied.

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# DETECTION OF $\alpha$ -GLYCOL GROUPS IN THIN-LAYER CHROMATOGRAPHY ON SILICA GEL

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Thin-layer chromatography [1,2], discovered in 1938 by N. A. Izmailov and M. S. Shraiber [3], has found widespread application in recent years for the separation of lipophilic substances [4-11]. This method has also been extended to certain hydrophilic substances (amino acids [12-14], amines [15]), but up to the present time it has not been used for the separation of polyhydroxy compounds, in particular, carbohydrates.\*

In the present work, which was undertaken in connection with a study of the chemistry of macrolide antibiotics, we investigated the possibility of detecting polyhydroxy compounds during chromatography in a thin layer of silica gel. The materials investigated were carbohydrates and related substances (glucose, lactose, glucosaccharin), polyhydric alcohols (ethylene and propylene glycols, glycerol, 3-methyl-1-hexyne-3,4-diol), and polyhydroxy acids (tartaric and 2,3-dihydroxy-2-methylpentanoic acid). The chromatography was carried out on plates (13 x 18 cm) covered with a layer KSK silica gel (150-200 mesh) mixed with gypsum and water (6 g of silica gel, 0.35 g of gypsum, and 15 ml of water). After the paste had been applied, the plates were dried in air for 6-12 hours and for 40 minutes at 104-106°. Reagents commonly used in paper chromatography for detection of the  $\alpha$ -glycol group were tested for detection of the polyhydroxy compounds on the chromatograms: a mixture of a 5% aqueous solution of silver nitrate with 25% ammonia (A) [17], and alkaline solution of sodium periodate and potassium permanganate (B) [18], lead tetraacetate (with subsequent spraying with rosaniline) (C) [19,20], and potassium periodate plus benzidine (D) [21].

We studied the dependence of the sensitivity of these reagents on both the nature of the substance being chromatographed and the developer system (see Table 1).\*\* The most sensitive reagent proved to be ammoniacal silver nitrate, which gave a distinct brown spot against a light background. A drawback to this reagent was the formation of a broad dark band (1-2 cm) at the frontal line, which made determination of substances with high  $R_f$  values difficult. The method based on oxidation of lead tetraacetate in chloroform was somewhat less sensitive. In certain cases (2,3-dihydroxy-2-methylpentanoic acid, glucosaccharin), the resulting white spot on a brown background became clearer upon subsequent treatment of the chromatogram with rosaniline. The mixture of sodium periodate and potassium permanganate in an alkaline solution detected the  $\alpha$ -glycol group by the appearance of white spots against a rose-colored background. However, these spots developed relatively slowly (only after 40-50 minutes in a number of cases). The least suitable method was that based on oxidation of potassium periodate and subsequent spraying with benzidine. Although, as is well known, this method is very sensitive for carbohydrate detection in paper chromatography, under the conditions of thin-layer chromatography the majority of the substances studied in this work could be detected only in amounts of 20-50  $\gamma$ .

The data presented in Table 1 shows that the most easily detectable substances were glycerol, glucose, lactose, and tartaric acid; the most difficultly detectable were the glycols and, in particular, the compounds with a branched chain and containing a tertiary hydroxyl group. The sensitivity of the detection reaction greatly depended on the developer system, and it varied within rather wide limits. This was apparently associated with the different sizes of spots (i.e., with differences in the concentrations of the substances after chromatography). We also established that the systems ethyl acetate-methyl benzoate-formic acid and butanol-ethanol-formic acid, which are used in paper

\* The paper of Stahl and co-workers [16] on the separation of carbohydrates in a thin layer of kieselguhr appeared while the present article was being prepared for printing.

\*\* The table shows the smallest amount of the material detectable as a clear spot. The  $R_f$  values are averages of four determinations. As a rule, deviations between individual determinations did not exceed  $\pm 15\%$ .

chromatography for the development of, respectively, acids and carbohydrates, are essentially inapplicable in thin-layer chromatography. The methyl benzoate and butanol components of the mentioned systems are strongly adsorbed by silica gel (they could not be removed even by prolonged drying at 105-110°),\* and this created a background which interfered with detection of the substances.

TABLE 1. Minimum Amounts of the Substances (in  $\gamma$ ) Detectable with the Different Systems

Compound	R <sub>f</sub>	Reagents			
		A	B	C	D
Methanol - chloroform (1 : 9)					
Ethylene glycol	0.3	10	10	50	50
1,2-Propylene glycol	0.35	10	20	40	40
Glycerol	0.1	2	4	10	6
3-Methyl-1-hexyne-3,4-diol	0.5	20*	10	40	50
Glucosaccharin	0.15	20	40	50	40
2,3-Dihydroxy-2-methylpentanoic acid	0.05	12	—	—	—
Ethanol - water (95 : 5)					
Tartaric acid	0	1.5	5	10	10
Glucose	0.7	1.5	15	20	15
Lactose	0.5	1.5	15	20	20
Glycerol	0.8	4	15	20	15
Glucosaccharin	0.8	20	40	32	50
2,3-Dihydroxy-2-methylpentanoic acid	0.5	20	40	32	50
Ethanol - acetic acid - water (60 : 30 : 10)					
Tartaric acid	0	2	5	10	10
Glucose	0.7	2	15	20	50
Lactose	0.6	2	10	20	50
Glycerol	0.8	4	20	15	50
Glucosaccharin	0.8	20	40	40	50
2,3-Dihydroxy-2-methylpentanoic acid	☛	20	40	40	50
Ethanol - 25% ammonia - water (85 : 5 : 10)					
Tartaric acid	0.05	2	5	10	8
Glucose	0.4	2	12	20	25
Lactose	0.1	2	10	16	32
Glycerol	0.7	3	10	20	16
Glucosaccharin	0.15	15	40	32	40
2,3-Dihydroxy-2-methylpentanoic acid	0.8	15	40	32	40

\* Detected as white spots, which were due to the formation of an ammonia complex of silver acetylde.

\*\* Did not give a clear spot.

Table 1 also presents some data on the separating ability of the developer systems studied in this work. The chloroform-methanol (9:1) mixture proved to be the most suitable system for the separation of polyhydric alcohols. The ethanol-water (95:5) and ethanol-ammonia-water (16:1:3) systems were the best for separation of glucose, lactose, and the hydroxy acids.

Our results show that thin-layer chromatography on silica gel is suitable for separation of polyhydroxy compounds, but the  $\alpha$ -glycol group of these substances can be detected only at relatively high concentrations. The sensitivity of all reagents was 2-5 times less than in paper chromatography. This can probably be explained by the

\* Drying at 95-100° for 1.5-2 hours was sufficient for the remaining systems, which are shown in Table 1. As a rule, development of the chromatograms occupied from 2 to 4 hours.

formation of strong hydrogen bonds between the hydroxyl groups of the substances investigated on the oxygen atoms of the silica gel.

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# ON TWO CONFIRMATIONS OF CERTAIN TRANSITION METAL COMPLEXES

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In the present communication, we consider the possibility of the existence of two conformations (nonequivalent equilibrium configurations) of certain octahedral complexes of the transition metals. These are analogous in principle to conformations of organic compounds, which have been widely investigated.

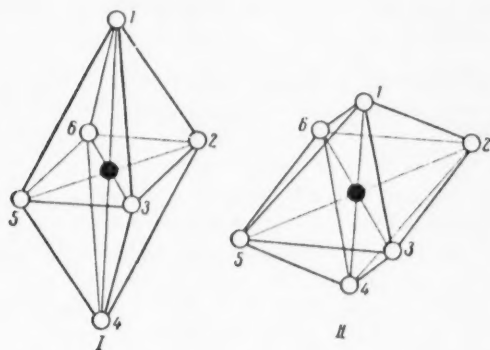


Fig. 1

It is known that the equilibrium positions of the ligands in six-coordinated transition metal complexes deviate, generally speaking, from positions at the vertices of a regular octahedron, even when all ligands are identical. This internal asymmetry of the  $\psi$ -shell of d electrons of the central atom, and, as previously shown [1,2], it is especially great for  $d^9$  electronic configurations (Cu(II), Ag(II), Au(II),  $d^4$  (Cr(II), Mn(III), Mo(II), W(II), Re(III))—in low-spin states. Naturally, two types of equilibrium configurations which are not equivalent are possible in these cases. The equilibrium octahedron is tetragonally distorted in both cases, but in one of them one diagonal of the octahedron is longer than the other two (a lengthened or elongated octahedron, Fig. 1, I), while in the other it is shorter (a shortened or oblate octahedron, Fig. 1, II). These two equilibrium configurations correspond to minima in the potential energy surface of the complex, and, since they are nonequivalent, we shall designate them as configurations I and II, respectively. We shall show that there are essential differences between them, which lead to interesting consequences.

The most essential characteristic of a conformation is its energy. In calculating the energy of complexes, we usually represent it as the sum of two components [2]: the energy of interaction of the optical electrons of the central ion\* with the ligands and the energy of the remaining interactions in the skeleton of the complex. While the first energy component may be calculated quite accurately, the second component is approximated by means of force constants. It is assumed that the potential well for the ligands is strictly symmetrically parabolic (the vibrations of the ligands are harmonic). In this approximation, the energies of the two conformations I and II are the same. However, if we take into account dissymmetry which gives a cubic term in the expansion of the potential energy for displacements of the ligands from equilibrium positions (i.e., anharmonic vibrations), then the energies obtained for two conformations are different. Since the correction introduced into the energy by anharmonicity does not exceed a few per cent, this must be the order of magnitude of the difference in energy between the two conformations. An estimate shows that the energy of conformation II is higher than the energy of conformation I by a few per cent of the specific energy of formation of the conformation—the decrease in energy during the transition from a regular to a distorted octahedron (20-30 kcal/mole)—this difference is of the order of 1 kcal/mole. This estimate of the difference in the energies of conformations I and II is very rough; however, this does not detract from the following qualitative conclusions.

\*The over-all picture and results obtained by the approximate molecular orbital method are similar.

With such an energy difference, the concentration of a complex in conformation I under equilibrium conditions will be approximately ten times the concentration in conformation II, as is easily calculated by means of Boltzmann distribution.

Other important characteristics of the conformations are the magnitude of the internal asymmetry  $\xi = 2(R_{01} - R_{02})$  (the difference in the lengths of the two diagonals), the energy and symmetry of the electronic states, and the frequency of hindered motions—transitions between three equivalent states with different directions of asymmetry (along the diagonals 1-4, 2-5, and 3-6). Methods for the determination of these values, the general equations, and calculations for some aquo complexes have been given by us in previous communications [1-3]. By means of these equations it is also possible to determine the height of the energy barrier for each conformation—the difference between the energy of the complex as a regular octahedron and the energy for the given conformation. Knowing the heights of the energy barriers, it is possible to determine the frequency of the transitions between conformations and the lifetime of each conformation in a manner similar to that by which these values were determined for hindered motions [3].

Values so calculated for the characteristics of the conformations in the case of  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  are: magnitude of the internal symmetry  $\varphi = 2(R_{01} - R_{02})$ , 0.8 Å (I) and -0.8 Å (II); difference in the energies of conformations I and II, ~1 kcal/mole; ratio of concentrations, II: I, at equilibrium at ordinary temperatures, ~0.1; height of the potential barrier between conformations, ~15 kcal/mole (I) and ~14 kcal/mole (II); lifetime in the ground state, ~4 days (I) and ~3.3 hours (II); difference in energies of the bonds of ligands 1 and 2, ~-15 kcal/mole (I) and ~15 kcal/mole (II).

It is apparent from these data that the lifetime of a conformation is long enough that it is possible to consider each conformation as an independent chemical entity (in calculating the lifetimes of the conformations, we assumed that the corresponding frequency of vibration of the complex is  $250 \text{ cm}^{-1}$ ).

The results of an approximate calculation of the difference in the bonding energies of the ligands at the long and short diagonals, respectively, are interesting. This difference may be obtained from the explicit form of the energy of the optical electrons in the ligand field [1,2] taking into account the correction for the difference in the changes in energy of the residue upon removing ligands 1 and 2. As would be expected, the ligands at the long diagonals are bound more weakly than those at the short diagonals; in the case of  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ , the difference in these bonding energies is of the order of 15 kcal/mole. Thus, for configuration I the two ligands in transpositions 1 and 4 are bonded significantly more weakly than are the remaining four ligands in positions 2,3,5, and 6, while for configuration II these latter four ligands are bonded more weakly than are the first two. While both the close and the remote ligands of conformation II are bonded more strongly (by the order of 5 kcal/mole in the case of  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ), than are the corresponding close and remote ligands of conformation I (at the same time, the energy of conformation I is no higher than that of conformation II, since in the latter there are four remote, weakly bonded ligands, while in the case of I there are only two). This is one of the most fundamental differences in the two conformations, and it is undoubtedly reflected in the reactivities of these complexes.

Let us consider an example. We shall assume that a substitution reaction of a Cu(II) complex with identical ligands (for example, an aquo complex) takes place by an  $\text{S}_{\text{N}}1$  mechanism. Then, in the case of conformation I, ligands 1 and 4 must inevitably be replaced first owing to their substantially weaker bonding. This apparently explains the clearly expressed tendency of Cu(II) toward the formation of trans-substituted complexes. It is possible that with the removal of both ligands 1 and 4, replacement of only one of them is sufficient for stabilization of the complex. Pyramidal coordination, which is also characteristic of Cu(II) complexes, is thereby formed. (These same considerations are probably also applicable to an  $\text{S}_{\text{N}}2$  mechanism.) As regards conformation II, both trans and cis substitution are possible in principle. But, in the first place, conformation II is less reactive than I owing to the stronger bonding of the individual ligands; in the second place, its concentration is appreciably lower at ordinary temperatures. Moreover, cis substitution is hindered by the fact that after the removal of one weakly bonded ligand, for example, 2 (Fig. 1, II), conditions are most favorable for the removal of the ligand in trans-position 5. If the substitution is stepwise, then if there is a sharp difference between the substituted and the substituting ligands, the latter will introduce a strong perturbation, which can convert the complex from conformation II to the more stable conformation I with subsequent trans-substitution. However, for certain reactions, it is apparently possible to create conditions such that cis substitution is obtained (an increase in the concentration of conformation II with an increase in temperature, substitution of ligands which are quasi-identical—labeled or identical in part—and which are bonded to the central atom, etc.).

Of the other possible developments of the existence of two conformations, we may mention relaxation phenomena, which lead to additional absorption of ultrasonic waves when such are passed through a solution of a complex



compound (a similar additional absorption of ultrasonic waves has been observed for conformations of organic compounds [4]). Some possibilities for a difference between two conformations are also represented by data on the absorption of light [5].

Investigation of the questions arising in the present communication await development of the investigation and experimental confirmation.

In conclusion, we acknowledge our deep appreciation for valuable discussions with Academician A. A. Grinberg and Prof. A. V. Ablov.

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## THE INTERACTION OF SULFUR WITH RUBBER UNDER THE INFLUENCE OF $\gamma$ -RADIATION

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In our earlier work [1], it was shown that sulfur adds to rubber under the influence of  $\gamma$ -radiation; an increase in cross-linking is observed at temperatures above 80°, while at temperatures below 80°, the formation of cross-links in natural rubber (NR) decreases. The sulfur enters the polymer in the form of polysulfide groups which are capable of undergoing isotope exchange with radioactive elemental sulfur. The static strength is increased over that of the pure rubber vulcanizate, but the thermal stability is lower.

Since the process occurring during radiation vulcanization is considered to take place through a stage in which free radicals interact, it appeared of interest to trace the reaction of sulfur with rubber by means of electron paramagnetic resonance (e.p.r.). The spectra were obtained with a spectrometer with a high-frequency modulation in the range of 3 cm. The measurements were carried out over the temperature interval from -140° to +20°. The radiation dosage was 6-11 Mr at both +20° and -196°.

It was found that irradiation at +20° of NR and its mixture with 2% sulfur led to the formation of radicals giving identical spectra in the two cases ( $g = 2.003 \pm 0.003$ , width about 15 oe), and the radical concentration was  $(1-2.5) \cdot 10^{14}$ /mg. The radicals were distinguished by a high stability, and could be detected 30-45 days after the irradiation in concentrations of  $(0.05-0.1) \cdot 10^{14}$ /mg.

In accordance with generally accepted ideas, it can be assumed that the free radicals arising during irradiation of the rubber do so as a result of elimination of a hydrogen atom and rupture of  $-C-C-$  bonds in the molecular chains of the rubber. In addition to alkyl radicals, allylic radicals are also formed, and these are stabilized by conjugation of the free valence with the neighboring double bond. These are apparently long-lived polymer radicals.

When the irradiation was carried out at -196°, the spectrum of NR differed from the spectrum of the mixture of NR and sulfur; each spectrum comprised superimposed lines, which indicates the presence of several types of radicals. The line width for NR was 28 oe, and that for the NR-sulfur mixture was 30 oe; the  $g$  factor was  $2.003 \pm 0.003$  in both cases. The initial concentration of free radicals was  $(4.9 \pm 0.7) \cdot 10^{15}$ /mg for the pure rubber and  $(2.6 \pm 0.6) \cdot 10^{15}$ /mg for the NR-sulfur mixture. By analogy to benzene, the inhibiting effect of the sulfur can be ascribed to delocalization of the electron in the eight-membered ring of the sulfur molecule.

When a sample irradiated at -196° was warmed in room-temperature air for 1-1.5 minutes, the spectrum became precisely the same as the spectrum of the long-lived radicals obtained by irradiation of similar samples at +20°. It follows from this that radicals with different stabilities, both long-lived and short-lived, were formed during irradiation at -196°. The lifetimes of the short-lived radicals at room temperature are measured in seconds. We also investigated the changes in radical concentration and in the nature of the lines during heating of the sample from -196° to +20° in vapors of boiling liquid nitrogen. This temperature interval was covered in steps of 6-7°. The temperature was raised to the given point, the sample was held at this temperature for a specific length of time (in different cases, the holding time was 30 seconds, 2 minutes, 5 minutes), the sample was then chilled to -140°, and the spectrum was recorded at this temperature.

Fig. 1 shows the drop in radical concentration occurring as a result of an increase in temperature with a holding time of 5 minutes. It is apparent that there is no change in the spectrum during heating from -196° to -120°. The

interval of intense destruction of radicals corresponds to the glass region of the rubber (temperatures from  $-80$  to  $-50^\circ$ ). This means that the reactivity of the radicals sharply increases in the region in which there is a rapid change in the mobility of the individual units of the molecular chain. Within this temperature region there is also a substantial

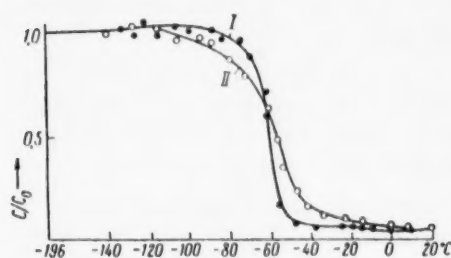


Fig. 1. Relative change in radical concentration during heating of the samples irradiated at  $-196^\circ$ : I) natural rubber; II) mixture of NR with 2% sulfur.

change in the form of the lines. While during heating of the irradiated NR only destruction of the original short-lived radicals can be detected (Fig. 2), the appearance of new short-lived radicals with a higher  $g$  factor is observed simultaneously with the destruction of the short-lived radicals (Fig. 3).

The picture one sees in this latter case can be interpreted in two ways: either at least two new species of radicals are formed during heating of the irradiated NR-sulfur mixture, or a single species is formed with an anisotropic  $g$  factor and containing an  $-S-S-$  group, which is analogous to the  $-O-O-$  peroxide group which has been established in the case of the irradiation of teflon in the presence of oxygen [2].

The concentration of the new radicals arising during heating of the irradiated mixture of natural rubber and sulfur changes as a function of the heating temperature along a curve with a maximum in the region of about  $-80^\circ$  (Fig. 4). This means that at this tem-

perature there is the most favorable ratio of the rate of formation of new radicals to the rate of their destruction, which provides the highest recorded concentration of radicals.

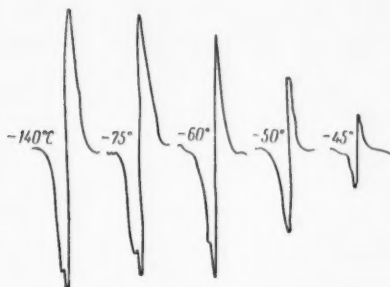


Fig. 2. Change in the spectrum of NR irradiated at  $-196^\circ$  during stepwise heating; the heating temperatures are indicated.

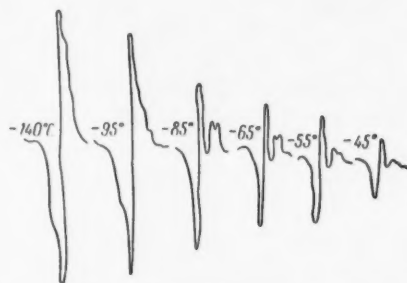
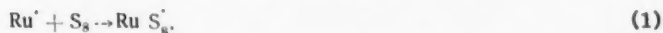
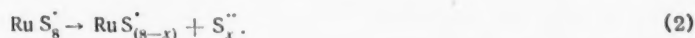


Fig. 3. Change in the spectrum of a mixture of rubber and 2% sulfur irradiated at  $-196^\circ$  during stepwise heating; heating temperatures are indicated.

The clearest of the additional lines characterizing the newly-formed radicals had a  $g$  factor of  $2.027 \pm 0.003$ . This value agrees with the value determined for sulfur radicals contained in the melt at  $200^\circ$  [3]. On the basis of the above, it may be assumed that the new radicals are formed as a result of the interaction of  $S_8$  sulfur molecules with polymer radicals of the rubber,  $Ru^\cdot$ , which are formed under the influence of the  $\gamma$ -radiation. Such an interaction cannot take place below the glass temperature. It is possible only at temperatures such that the molecular chains of the rubber acquire the necessary mobility, and the reaction includes opening of the eight-membered ring of the sulfur:



The polymer-sulfide radical,  $RuS_8^\cdot$ , can decompose further with the liberation of sulfur radicals:



Thus, the fundamental fact of the formation of sulfur radicals as a result of the interaction of polymer radicals with sulfur molecules at low (negative) temperatures has been recorded. Elemental sulfur apparently does not form radicals under the influence of  $\gamma$ -radiation, since in our experiments, irradiation of crystalline sulfur led only to the appearance of a weak signal, which could be ascribed to a lattice defect.

Radicals of the type  $\text{RuS}^{\bullet}(\text{S}-\text{X})$  have a longer lifetime than do  $\text{Ru}^{\bullet}$  polymer radicals, and  $\text{S}_x^{\bullet}$  radicals are more active. For this reason, the radical-destruction curve (Fig. 1) for the NR-S mixture encompasses a broader temperature region than does the analogous curve for pure rubber. The interaction of polymer radicals with each other and with rubber molecules leads to a three-dimensional cross-linked structure. The cross-linking effect appears in the temperature region in which, according to the e.p.r. data (Fig. 1), the most rapid disappearance of radicals during "freezing" of the irradiated rubber takes place.

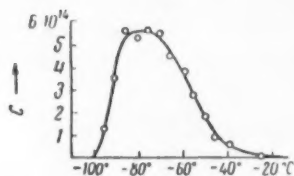


Fig. 4. Dependence of the concentration of short-lived radicals on heating temperature for the mixture of NR with 2% S irradiated at  $-196^{\circ}$ .

Sulfur decreases cross-linking during irradiation of rubber at low temperatures [1]. This action of sulfur could be a consequence of the above-described phenomenon of sulfur inhibition of the formation of polymer radicals.

The sulfur-containing polymer radicals formed by Reactions (1) and (2) could be stabilized by the formation of terminal cyclic groups, which also leads to a decrease in the formation of cross-linking bonds. Sulfur biradicals,  $\text{S}_x^{\bullet}$ , apparently take part in the cross-linking reactions, interacting with double bonds of the molecular chains. However, this interaction can also lead to the formation of intramolecular ring structures, which does not increase the number of cross-links. As already noted, the sulfur structures formed during the initial stages of irradiation (at a dose of up to 10 Mr) can undergo 70% isotope exchange with elemental sulfur labeled with  $\text{S}^{35}$ ; further irradiation decreases the ability to undergo exchange to 40% (at a dose of 50 Mr). Such a high degree of isotope exchange indicates the presence of linear polysulfide structures,  $\text{S}_x$ , where  $x > 1$ , in the vulcanizates investigated. As we have previously shown [1], the presence of these polysulfide structures substantially increases the static strength of radiation vulcanizates.

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# AN INVESTIGATION OF THE SYSTEM Mn - Si IN THE SILICON-RICH REGION

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In recent years a number of investigators have directed their attention to magnesium disilicide ( $\text{MnSi}_2$ ), which has semiconductor properties. At the same time, an analysis of the literature data, cited below, from an investigation of Mn-Si alloys casts doubt on the complete authenticity of the phase composition reported for the region of interest in this work. All of this, together with the results of preliminary microstructural investigations, dictated work in which the system Mn-Si would be carefully studied in the silicon-rich region.

a) According to the equilibrium diagram of the Mn-Si system, based on data from investigations [1,2] which are cited in the monograph by A. S. Berezhnoi [3], manganese disilicide is formed by a peritectic reaction:  $\text{liq} + \text{Si} \rightleftharpoons \text{MnSi}_2$  at about  $1144^\circ$ .

The existence of manganese disilicide was confirmed by Boren [4] on the basis of an x-ray investigation. According to his data,  $\text{MnSi}_2$  crystallizes with a tetragonal structure with constants of  $a = 5.51 \text{ \AA}$ ,  $c = 17.42 \text{ \AA}$ , and  $c/a = 3.16$ ; the space group is  $D_{4h}^{18}$ . The more recent investigation of Hansen [5] indicated a different scheme for the formation of the disilicide:  $\text{liq} + \text{MnSi} \rightleftharpoons \text{MnSi}_2$  at about  $1155^\circ$ .

According to the data of E. N. Nikitina [6,7], manganese disilicide has a coefficient of thermal e.m.f. of the order of  $80\text{--}120 \text{ } \mu\text{V}/^\circ\text{C}$  (depending on the purity of the initial material) at room temperature and an electrical conductivity of  $300\text{--}400 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ . The thermoelectric characteristics of  $\text{MnSi}_2$  change like those of metals with an increase in temperature: the electrical conductivity drops; the thermal e.m.f. increases [8]. This last paper presents the results of an investigation of the thermoelectric properties of alloys of the system Mn-Si in the range of 20 to 80 atom % Si. On the basis of the relationships obtained in this work, it was concluded that a new compound,  $\text{Mn}_2\text{Si}_3$ , exists in the region from MnSi to  $\text{MnSi}_2$ . However, this conclusion is not quite justified, since the author did not control the phase composition of the alloys nor their equilibrium.

In summarizing this literature survey, we feel it necessary to repeat our original conclusion that there is not sufficient basis for the phase composition cited in the literature for the indicated region of the system. Confirmation of this may be found in the complex nature of the dependence of the thermoelectric properties on composition [8], the contradictory data on the nature of the formation of the disilicide [3,5], the lack of original x-ray investigations of Mn-Si alloys [4], and the results of microstructural and thermal analysis [5] (Hansen refers to his own unpublished work).

b) The starting materials used were silicon, prepared by the method of Beketov (99.998% Si), and electrolytic manganese, which was given two preliminary refusions and which contained traces of Al, Si, and Cu and less than 0.001% Pb, Mo, Ti, and Co according to spectroscopic analysis. Preparation of the alloys was carried out as follows. First, for the purpose of constructing the corresponding phase diagram, fusion of the initial components in evacuated and sealed quartz ampoules was carried out by means of high-frequency heating. Then, in order to prepare samples having the required dimensions, the resulting alloys were placed in quartz ampoules of the necessary diameter and remelted in a resistance furnace. After careful stirring, the alloys were cooled in air. Since the conditions of preparation of the alloys were identical and since the decrease in the weight of the samples as compared to the weight of the initial mixture was small (about 0.2%), we believe that the deviation of the composition from that calculated is insignificant.

In order to bring the alloys to the equilibrium state, they were annealed in sealed quartz ampoules under argon at a temperature of  $1000^\circ$  for 200 hours and were cooled in the furnace.



The polished surfaces were etched with hydrofluoric acid to develop the structure. Thermal analysis was carried out both by means of differential recording of the heating curves of the equilibrium samples and by means of cooling curves. The sample and standard (silicon) were sealed in evacuated quartz Stepanov cells. The investigation was carried out over the temperature interval of from 600 to 1200°.

The x-ray phase analysis was accomplished with patterns obtained by the Debye method using chromium radiation.

The thermoelectric properties were measured at room temperature by a compensation scheme using a potentiometer. Measurement of the temperature dependence of the electrical conductivity was carried out under vacuum at temperatures up to about 800°.

c) A series of alloys with Manganese contents of from 46 to 55% were prepared by the method described above.

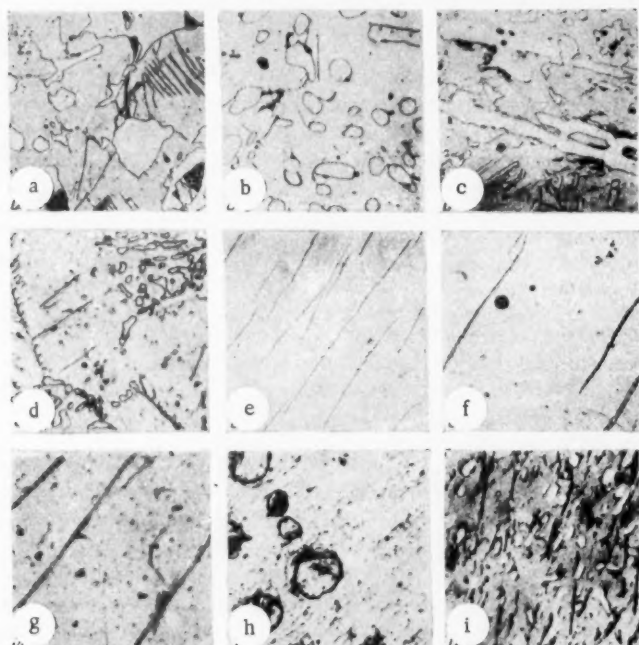


Fig. 1. Microstructures of Mn-Si alloys: a)  $\text{MnSi}_2$ , cast, 270X; b)  $\text{MnSi}_2$ , annealed, 270X; c) 46.4% Mn + 53.5% Si, cast 270X; d)  $\text{Mn}_3\text{Si}_5$ , cast, 270X; e)  $\text{Mn}_3\text{Si}_5$ , annealed, 270X; f)  $\text{Mn}_3\text{Si}_5 + 0.5\%$  Si, annealed, 270X; g)  $\text{Mn}_3\text{Si}_5 + 0.5\%$  Mn, annealed, 270X; h) 55.5% Mn + 44.5% Si, annealed, 270X; i) 50.5% Mn + 49.5% Si, annealed, 270X.

A preliminary investigation of the microstructure of samples having the composition  $\text{MnSi}_2$ , both cast and annealed, (Fig. 1, a, b) showed that it is not single phase and contains significant separation of silicon (differences in the structures of cast and annealed alloy, chiefly in the outlines of the silicon grains, were apparently associated with peculiarities in the crystallization of the eutectic which, as we shall see later, is bordered by the indicated composition). A detailed investigation of the microstructure of samples richer in silicon confirmed the correctness of the conclusion that the Mn-Si system has no phase of the composition  $\text{MnSi}_2$  and, secondly, that there are no phase transformations in the region of the initial silicon crystallization. The latter conclusion is confirmed by the structure of the cast alloy containing 53% Si (Fig. 1, c). A study of the structure of alloys richer in manganese (Fig. 1, d-h) provided a basis for the assumption that there is a transformation in this part of the system which results in homogeneity for the sample containing 46% Si (Fig. 1, d, e). This composition corresponds to a stoichiometric ratio of 3:5 of the components.

A detailed study of alloys in the neighborhood of the above composition established that the compound  $\text{Mn}_3\text{Si}_5$  has a narrow region of homogeneity corresponding to a solution of about 0.5% excess silicon and manganese atoms in the compound (Fig. 1, f, g).

The results of differential thermal analysis during heating of the equilibrium samples and cooling of the alloys together with the data from the x-ray structural investigation permitted us to construct the phase diagram for part of the Mn-Si system (Fig. 2). The crosses mark the thermal effects found by Hansen [5], which, as is apparent from Fig. 2, supplement our results beautifully. It follows from this diagram that the compound  $\text{Mn}_3\text{Si}_5$  is formed by a peritectic reaction from manganese monosilicide and the liquid:  $\text{liq} + \text{MnSi} \rightleftharpoons \text{Mn}_3\text{Si}_5$ , at  $1159^\circ$ . The eutectic of this compound with silicon corresponds to a Si content of about 49% (Fig. 1, i), and it melts at a temperature  $10^\circ$  lower (about  $1149^\circ$ ). The composition of the compound is very close to the composition of the liquid phase corresponding to the invariant peritectic reaction. This establishes the fact, which follows from the microstructural analysis, that the process by which the compound  $\text{Mn}_3\text{Si}_5$  is formed takes place chiefly during crystallization (compare d and e, Fig. 1), and the cast samples gave no photographs characteristic of quenched peritectic transformations.

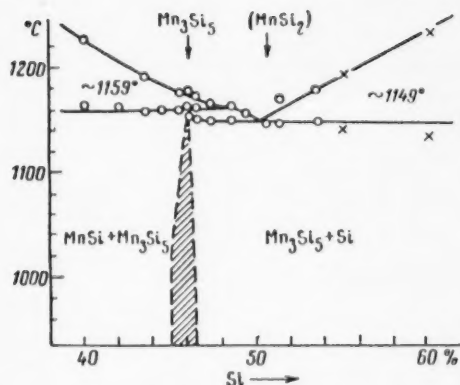


Fig. 2. Phase diagram for part of the Mn-Si system according to our data.

The basic conclusion reached on the basis of the microstructural investigations and the thermal analysis is that the compound  $\text{MnSi}_2$  does not exist in the Mn-Si system and that a phase richer in manganese than  $\text{Mn}_3\text{Si}_5$  does exist. This conclusion is confirmed by x-ray phase analysis data; the x-ray photographs showed additional lines where, according to the microstructural investigations, separation of a second phase (MnSi and silicon) took place.

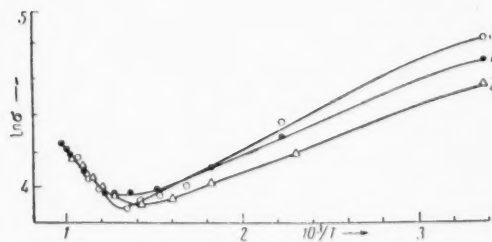


Fig. 4. Temperature dependence of the electrical conductivity of samples in the region of the solid solution based on  $\text{Mn}_3\text{Si}_5$ . 1) 53.99% Mn, 2) 54.51% Mn, 3) 53.45% Mn.

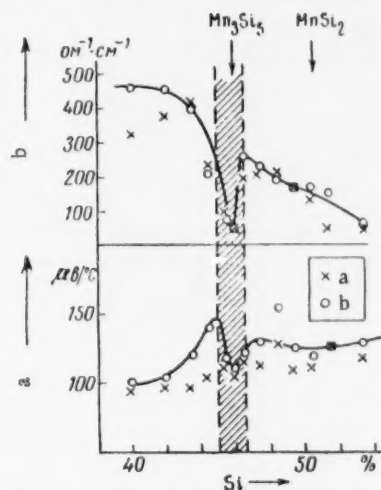


Fig. 3. Isotherms of thermoelectric properties of Mn-Si alloys in the region of the compound  $\text{Mn}_3\text{Si}_5$ : a) cast, b) annealed.

The specific electrical conductivity and the coefficient of the thermal e.m.f. were measured for all of the alloys prepared, both cast and annealed. The resulting values are plotted graphically as a function of composition (Fig. 3). It is clear from these graphs that the complex nature of the dependence of the thermoelectric properties in this region of the system [8] is due to the presence of a homogeneous region based on the compound  $\text{Mn}_3\text{Si}_5$ . Solution of the manganese and silicon atoms in excess over the stoichiometric composition, which is probably connected with the formation of a defect lattice by removal of atoms of the other kind, is accompanied by the appearance of additional current carriers. Evidence of this is the increase in electrical conductivity within the limits of the solid solution. Simultaneously, there is some increase in the thermal electromotive force.

The change in the thermoelectric characteristics in the two-phase regions is due to the influence of the second



phases of different natures. The temperature dependence of the electrical conductivity was measured for three samples from the  $Mn_3Si_5$  solid solution region. The results are plotted in Fig. 4. A metallic dependence,  $\sigma = f(1/T)$ , was exhibited by all three samples up to a temperature of the order of 500°; at higher temperatures, the values fell close to the same straight line. The activation energy of the current carriers, calculated from the slope of this line, was about 0.2 ev.

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THE USE OF ION-EXCHANGE CHROMATOGRAPHY  
IN RADIOACTIVATION ANALYSIS OF TRACE IMPURITIES  
IN SILICA\*

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One of the most sensitive methods for the determination of trace impurities in ultrapure materials is radioactivation analysis. The identification and quantitative determination of activated trace impurities are usually carried out either with separation and purification of the radioactive isotope, frequently in the presence of an inactive isotope carrier, or without such separation and purification (or with preliminary separation into groups in the event of analysis for more than one trace element). However, both of these methods have a number of disadvantages which limit their use. The method in which analytical chemistry procedures are used is very laborious owing to the necessity of carrying out radiochemical purification operations, and, therefore, it is very lengthy if the separation of a large number of elements is required. The method of  $\gamma$ -spectrometry also has its limitations. It cannot be used for the determination of purely  $\beta$ -emitters; the low resolving power of  $\gamma$ -spectrometers does not permit analysis of complex mixtures; owing to the presence of Compton scattering, the sensitivity of the determination of any trace impurity depends to a great extent on the presence of other impurities [1,2].

In the present work, which was devoted to the determination of trace impurities in silica by neutron activation analysis, separation of the mixture of activated trace impurities was carried out by ion-exchange chromatography, which possesses a number of advantages as compared to the usual analytical methods. Reliable and rapid separation of the trace elements in a radiochemically pure form from a complex mixture of trace impurities can be accomplished by means of ion-exchange chromatography. With the correct choice of conditions for absorption and elution of the elements separation by means of ion-exchange resins is quantitative. It is possible to use a microcolumn for the separation of trace amounts of the elements, and this considerably accelerates the separation process and decreases losses. In the present work, the amounts of elements separated were determined from the amounts of carriers, the addition of which was necessary to decrease the loss of activated trace impurities during solution of the sample and during certain analytical operations.

The silica samples to be analyzed were irradiated in sealed quartz ampoules. Solutions of standards of the elements being determined were placed in polyethylene ampoules and evaporated to dryness in a vacuum desiccator at 60°, after which the ampoules were sealed. The samples and standards were simultaneously irradiated in an atomic reactor. After irradiation, the samples were heated and washed with aqua regia to remove surface impurities. A solution of the carrier containing 10  $\mu$ g of each of the elements being determined was then added, and the sample was then decomposed with a mixture of hydrofluoric and nitric acids. After decomposition of the sample, the solution was evaporated three times with HF to remove the excess  $\text{HNO}_3$ . The last time the solution was evaporated to a volume of one or two drops, and was then diluted with an approximately equal volume of water. The resulting solution was passed through a polyethylene column having a diameter of 2 mm and packed with strongly basic AV-17 anion-exchange resin in the F' form (divinylbenzene content, 8-10%; particle size, 30-40  $\mu$ ; bed height, 5 cm). The elements were adsorbed in the column, forming negative fluoride complexes:  $\text{Sn}^{\text{IV}}$ ,  $\text{Mo}^{\text{VI}}$ ,  $\text{W}^{\text{VI}}$ ,  $\text{As}^{\text{V}}$ ,  $\text{Ta}^{\text{V}}$ ,  $\text{Sb}^{\text{V}}$ , and  $\text{Au}^{\text{III}}$ .

\* The work was initiated by Yu. V. Morachevskii.

According to the data of Faris [3], who made a detailed study of the adsorption of elements from hydrofluoric acid, these elements are strongly adsorbed from dilute solution, and adsorption decreases with an increase in the HF concentration. Therefore, it was possible to elute Sn, Mo, W, and As successively with a 17 N solution of HF, as shown in Fig. 1. However, good separation of these elements could be obtained only by the use of long columns operated under equilibrium conditions for the separation, which, however, greatly increased the time required for the separation. Therefore, these elements were eluted together, and were then separated in a column of  $50 \times 2$  mm filled with AV-17 anion-exchange resin in the Cl' form. Solutions of hydrochloric acid and mixtures of hydrochloric and hydrofluoric acids of various concentrations were used as eluents. The separation is represented schematically in Fig. 2.

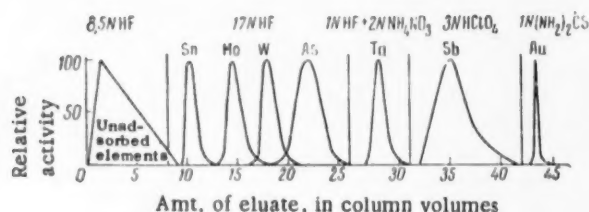


Fig. 1. Scheme of the separation of the elements adsorbed on anion-exchange resin in the F' form.

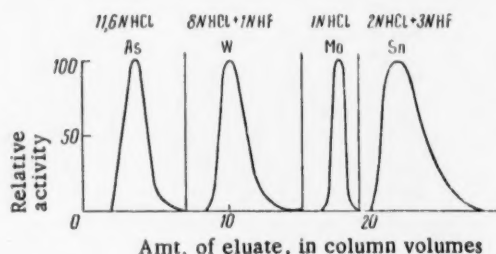


Fig. 2. Scheme of separation of the elements which were eluted together by 17 N HF.

The tantalum fluoride complex was adsorbed significantly more strongly, and it was difficult to elute with 17 N HF; hence,  $\text{NO}_3^-$  was added to the HF to accelerate the elution. The nitrate ion is adsorbed by the resin more strongly than is the  $\text{F}^-$  ion, and it rapidly eluted the tantalum. Antimony could be eluted with 3 N  $\text{HClO}_4$ , though with great difficulty, and gold, which was not eluted by any of the eluents enumerated above, was eluted with thiourea, with which it forms a stable positive complex.

The mixture of elements not adsorbed from hydrofluoric acid solution, was evaporated several times with hydrochloric acid and transferred to a  $90 \times 2$  mm column packed with Av-17 anion-exchange resin in the Cl' form. Elements forming negative chloride complexes were adsorbed in this column:  $\text{Cu}^{II}$ ,  $\text{Co}^{II}$ ,  $\text{In}^{III}$ ,  $\text{Ga}^{III}$ ,  $\text{Zn}^{II}$ ,  $\text{Cd}^{II}$ , and  $\text{Hg}^{II}$  [4]. Separation of these elements is represented schematically in Fig. 3. Elution of the elements was carried out with HCl solutions of different concentrations.

It should be pointed out that the copper chloride complex in 8-12 N HCl solutions has a constant and relatively low distribution coefficient. Elution of the column with such solutions shifted the copper zone and led to poorer separation between copper and cobalt. Therefore, immediately after removal of the unadsorbed elements with the minimum volume of 8 N HCl, separation of the cobalt and copper was carried out with 4 N HCl, and indium was then eluted with 11.6 N HCl.

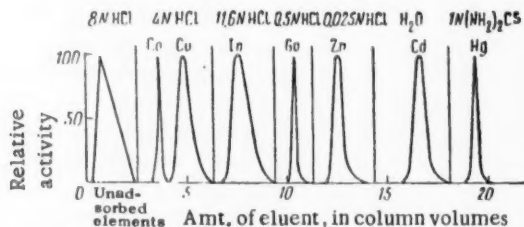


Fig. 3. Scheme of separation of elements adsorbed on the Cl' form of the anion-exchange resin.

Since the adsorption curves of gallium and iron are approximately the same, these elements were eluted to-

gether. The sensitivity of the radioactivation determination of iron is very low, especially with the comparatively short irradiation time used in the present work; therefore, the iron did not interfere with the determination of gallium.

TABLE 1

Element	Content, wt. %	Element	Content, wt. %
As	$5,2 \cdot 10^{-7}$	In	He not found
Au	$4,1 \cdot 10^{-8}$	Mo	$1,8 \cdot 10^{-6}$
Cd	$2,6 \cdot 10^{-6}$	Sb	$2,8 \cdot 10^{-5}$
Co	$2,0 \cdot 10^{-6}$	Sn	$5,9 \cdot 10^{-5}$
Cu	$3,8 \cdot 10^{-7}$	Fa	$5,4 \cdot 10^{-6}$
Ga	$6,2 \cdot 10^{-7}$	W	$4,8 \cdot 10^{-8}$
Hg	$5,1 \cdot 10^{-8}$	Zn	$5,1 \cdot 10^{-6}$

When necessary, gallium and iron can easily be separated with a cation-exchange resin [5]. The chromatographic scheme developed here was applied to the determination of trace elements in samples of silica. Fractions with the appropriate elements were then dried, and their activity was measured with an end-window counter. The time required to carry out the complete separation cycle, not counting the time for decomposition of the sample, was approximately 4 hours. Separation of the standard was carried out by the same scheme and in the columns.

The radiochemical purity of the elements after separation was checked by  $\gamma$ -spectroscopy and by determining the half-life of the activated isotopes. The experiment showed that the majority of the elements are radiochemically pure after separation.

By way of example, Table 1 shows the results of an analysis of one of the silica samples, which was irradiated for 10 hours in a neutron stream of  $10^{14}$  neutrons/sq cm/sec.

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# A STUDY OF THE INTERACTION OF AQUEOUS POTASSIUM METANIOBATE WITH OXALIC ACID

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Oxalic acid solutions of niobium and tantalum are rather important both in the radiochemistry and in the analytical chemistry of these elements. They have recently attracted the attention of investigators from the point of view of their use in the industrial separation of niobium from tantalum and other associated elements [1-3]. However, up to the present time very little attention has been given to the study of these solutions, nor have the composition of the complexes formed in the solution, their instability constants, their limits of existence, and stability with respect to pH been established. There is no experimental proof of the sign of the charge of these complexes, etc. All of this served as a basis for the present work.

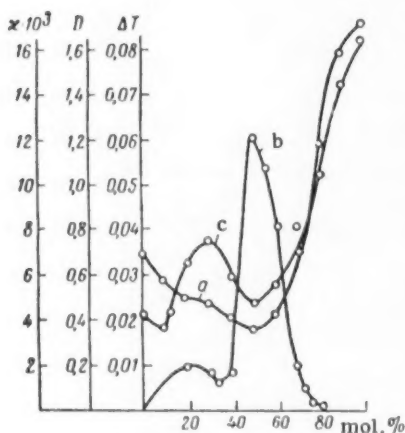


Fig. 1. Change in the electrical conductivity (a), optical density (b), and freezing point (c) in an isomolar series in the system  $\text{KNbO}_3\text{--H}_2\text{C}_2\text{O}_4\text{--H}_2\text{O}$ .

ratio of  $\text{KNbO}_3$  to  $\text{H}_2\text{C}_2\text{O}_4$  of 1:0.5. Hence, it may be concluded that the first stage of the interaction of potassium metaniobate with oxalic acid takes place according to the reaction:



This was also confirmed by the results of the pH determinations, which are presented in Fig. 3. The solution was transparent at the 1:1 point in all series (Fig. 2b). Equation (3) may also be discarded on the basis of the series of pH determinations. The pH was close to 4 at the 1:1 point of all solutions studied; i.e., the solutions were weakly acidic, while according to Eq. (3) the pH at this point should be slightly on the basic side. In order to confirm our

Physicochemical analytical methods were used to study the system  $\text{KNbO}_3\text{--H}_2\text{C}_2\text{O}_4\text{--H}_2\text{O}$ , and both isomolar series and series with a constant concentration of potassium niobate were studied. Electrical conductivity, optical density, turbidity, freezing point depression, viscosity, pH, and diffusion coefficients were determined with solutions of this series. Niobium-95 was used as a label in the measurements of diffusion coefficients. It is apparent from Figs. 1, 2, and 3 that when the data obtained by the above methods are plotted as composition-property graphs, the resulting curves have two extremums, one at a mole ratio of  $\text{KNbO}_3$  to  $\text{H}_2\text{C}_2\text{O}_4$  of 1:0.5 and the second at a ratio of 1:1. The reaction of potassium metaniobate with oxalic acid at a mole ratio of 1:1 can be represented by the following equations:



However, only Eq. (2) is acceptable according to our data. As a matter of fact, Eq. (1) may be discarded on the basis that the niobic acid formed in accordance with this equation is not capable of independent existence, and should precipitate. But the results of the turbidity and viscosity determinations and the data from the cryoscopic and diffusion coefficient measurements showed that maximum precipitation occurred at a mole



hypothesis, we carried out paper electrophoresis with 1:1 solutions. In conformity with Eq. 1, it was found that all of the niobium migrated to the anode; i.e., the niobium was a component of the negatively charged particle, while, according to Eq. (3), it should be a component of the positively charged particle or, in the event that the niobium formed a neutral complex, there should be no over-all migration. However, since the results of the diffusion coefficient measurements in this system revealed no interaction at the 1:1 point, but did indicate reaction at a ratio of approximately 1:2, we decided to confirm our results by means of a calculation. With this aim, we also measured the self-diffusion coefficient of potassium metaniobate. The value obtained was  $1.478 \cdot 10^{-5}$  sq cm/second at 25° and concentration of about 0.03 mole/liter. Since the self-diffusion coefficient of the complex was  $1.238 \cdot 10^{-5}$  sq cm/second under the same conditions, we attempted to evaluate the molecular weight of this complex using the approximate formula due to Euler,  $D\sqrt{M} = D_1\sqrt{M_1}$ . The calculation led to a molecular weight of 199.7, which is reasonably close to the value of 213, which corresponds to the theoretical value for the ion  $[\text{NbO}_2\text{C}_2\text{O}_4]^-$ . Thus, the composition of the complex is also confirmed by the self-diffusion measurements. It must be pointed out that the composition of the complex does not change up to a ratio of  $\text{KNbO}_3$  to  $\text{H}_2\text{C}_2\text{O}_4$  of 1:10, as is apparent from Fig. 2c. The complex formed at a pH of 2 is apparently in solution in a highly hydrated state, and this is reflected in a decrease in the values of the self-diffusion coefficients.

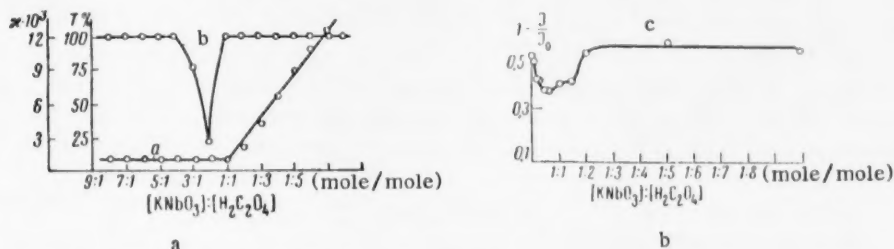


Fig. 2. Change in the electrical conductivity (a), transparency (b), and diffusion coefficient (c) in the system  $\text{KNbO}_3\text{--H}_2\text{C}_2\text{O}_4\text{--H}_2\text{O}$  for the series in which the total concentration of components was varied.

In order to confirm this proposition, we determined the self-diffusion coefficients in this system at a ratio of  $\text{KNbO}_3$  to  $\text{H}_2\text{C}_2\text{O}_4$  of 1:1 to 1:10 and a constant pH of 1.8. The experiment showed that at all potassium niobate-to-oxalic acid ratios studied, the self-diffusion coefficient of the resulting ion was constant and close to the value cited above. Thus, it may be considered proved that at all  $\text{KNbO}_3\text{:H}_2\text{C}_2\text{O}_4$  ratios studied, only one compound is formed, and the composition of this compound is given by the formula  $\text{K}[\text{NbO}_2\text{C}_2\text{O}_4]$ .

Using the data obtained in the study of the optical density of solutions in the isomolar series, we evaluated the instability constants of the complexion. The value obtained was  $8 \cdot 10^{-4}$ . Finally, it should be remarked that none of the methods used in the present work revealed the presence in the solutions of a compound with an Nb: $\text{H}_2\text{C}_2\text{O}_4$  ratio of 1:3, which would correspond to the formation of the salt described by Russ [4].

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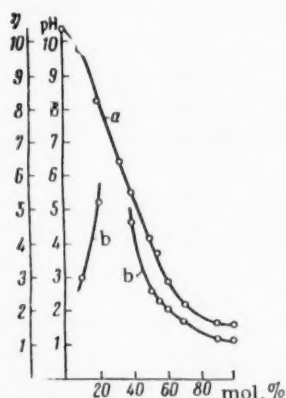


Fig. 3. Change in pH (a) and viscosity (b) in the system  $\text{KNbO}_3\text{--H}_2\text{C}_2\text{O}_4\text{--H}_2\text{O}$  for the isomolar series.

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

## HYDROGENATION OF CERIUM - MAGNESIUM ALLOYS

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(Presented by Academician I. I. Chernyaev, April 29, 1961)

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That hydrogen is absorbed by cerium-magnesium alloys was established by Sieverts and Roell [1]. These authors showed that the absorptive capacity of cerium, 214 cc/g, was practically unchanged by the addition of small amounts of magnesium; when cooled in an atmosphere of hydrogen, alloys containing 5.3 and 12.5% Mg took up 165.0 and 190.1 cc of hydrogen per gram of cerium, respectively.

The existence of cerium hydrides having the compositions  $CeH_2$  and  $CeH_3$  (absorption of 160 and 240 cc of hydrogen, respectively) has recently been proved. These hydrides were obtained by the reaction of cerium with hydrogen at room temperature [2,3]. Both of these hydrides, and especially  $CeH_3$ , are unstable in moist air [4]. The reaction of metallic magnesium with hydrogen yields magnesium hydride in the form of a white powder which is relatively stable toward moisture and air [5]. However, the hydrogenation of magnesium requires the use of elevated temperature and pressure and special catalysts.

Since experiments on the preparation of magnesium and cerium hydrides of constant composition had proved successful, we carried out the hydrogenation of cerium-magnesium alloys over a wider interval of magnesium concentration than had been investigated by Sieverts and Roell. The starting materials were cerium containing 97.75% Ce, 0.75% Nd, 0.4% Pr, 1.0% La, and 0.05% Fe and refined magnesium containing not less than 99.9% magnesium. Alloys containing up to 85 atm % Mg were prepared by alloying a weighed amount of metallic magnesium with an alloy having the composition of the compound  $Mg_3Ce$  (34.24% Mg) in corundum crucibles under a layer of LiCl-KCl flux (53.9% wt. % LiCl).

The hydrogenation was carried out at room temperature and a hydrogen pressure of 0.5 to 1 atm. The apparatus was one which had previously been used for the hydrogenation of cerium [3]. Both cast samples and samples which had been given a preliminary heat treatment were used. The heat treatment appreciably accelerated the absorption of hydrogen.

The hydrogen content of the hydrogenated alloys was determined by measuring the hydrogen evolved when a weighed portion of the material was reacted with hydrochloric acid. Absorption of hydrogen by the alloys began after different induction periods, which increased significantly with an increase in the magnesium content of the alloy. Samples 13, 14, and 15 could be hydrogenated only after activation by a preliminary heat treatment.

However, it should be noted that there was no regular change in the length of the induction period, the hydrogenation time, or the amount of hydrogen absorbed by the alloys with a change in composition (Table 1, Fig. 1). This is apparently associated with the great sensitivity of these properties toward a change in the structure of the solid solutions in accordance with the magnesium-cerium phase diagram. Hydrogenation of alloys with a magnesium content greater than 30% was accompanied by splitting of the original pieces along cleavage planes into regular, rectangular forms with a lustrous black color. These pieces were brittle and were easily ground to a fine powder.

As may be seen from the hydrogenation indices (Table 1), very small additions of magnesium to cerium (up to 5 atm %) cause almost no change in the composition of the cerium hydride, and are reflected only by a significant increase in the induction period and in the hydrogenation time. Hydrogenation of alloys containing more than 5 atm. % magnesium took place only after an even greater induction period; as a rule, hydrogen absorption had not begun after 6 hours, and saturation was reached only after several days with alloys containing 46-66 atm % Mg. In general, pieces of alloys of this composition did not hydrogenate, but hydrogenation did take place after they were powdered.



Analysis of the products of the hydrogenation of the cerium-magnesium alloys (Table 1) showed that when up to 30 atm % Mg was added to the cerium, the hydrogen content did not correspond to complete hydrogenation of both the cerium and the magnesium. Starting at 30 atm % Mg, the compositions of the hydrogenated alloys corresponded to saturation absorption of hydrogen by each of the metals separately; i.e., for an alloy  $Mg_mCe_n$ , the composition of the hydrogenation product was close to that expressed by  $Mg_mH_{2m}Ce_nH_{3n}$ . In particular, the alloy containing 46% Mg gave a hydride with a composition close to that of the "double hydride"  $MgCeH_5$ . Beginning with alloy 13 (50% Mg), hydrogen absorption decreased sharply, and it ceased completely with the alloy corresponding to the composition  $Mg_3Ce$  (34.24 wt. % Mg).

TABLE 1. Composition of Products from the Hydrogenation of Cerium-Magnesium Alloys

Expt. no.	Alloy comp.		Induc. period, min.	Hydrogenation time	Hydrogen content			Formula of hydride
	Mg, at. %	Mg, wt. %			per g hydride, ml	per g cerium, ml	at. %	
1	0	0	1-3	1-4 min.	234,9	240,0	75	$CeH_3$
2	0,1	0,002	90	2,0 hrs.	233,2	238,9	74,79	$CeMg_{0,0011}H_{2,97}$
3	0,2	0,004	35	2,0 »	232,7	237,6	74,77	$CeMg_{0,00218}H_{2,98}$
4	0,5	0,10	10	>6 »	233,5	237,5	74,76	$CeMg_{0,0059}H_{2,98}$
5	1,0	0,18	15	2,5 »	233,5	238,9	74,68	$CeMg_{0,01039}H_{2,99}$
6	5,0	0,90	180	>6 »	237,3	241,2	74,48	$CeMg_{0,052}H_{3,07}$
7	10,0	1,89	>240	>6 »	242,0	251,0	74,41	$CeMg_{0,111}H_{3,23}$
8	20,0	4,15	>240	>6 »	240,6	256,8	72,11	$CeMg_{0,240}H_{3,23}$
9	30,0	6,92	>240	>6 »	282,4	319,6	72,97	$CeMg_{0,43}H_{3,86}$
10	35,0	8,55	20	>6 »	288,8	329,3	72,52	$CeMg_{0,538}H_{4,060}$
11	40,0	10,37	>240	>6 »	302,4	347,2	72,90	$CeMg_{0,665}H_{4,48}$
12	46,0	12,88	>180	>1,5 days	315,0	366,4	71,66	$CeMg_{0,852}H_{4,682}$
13	50,0	14,79	>240*	>6 »	272,8	341,5	67,37	$CeMgH_{4,13}$
14	60,0	20,58	10*	>6 »	320,2	414,8	67,17	$CeMg_{1,493}H_{5,10}$
15	66,66	25,77	40*	~2 »	284,6	393,4	61,98	$CeMg_2H_{4,89}$
16	75,0	34,24	not hydrogenated					

\*After heat treatment at 400°.

Upon comparing these results with the phase diagram of cerium-magnesium alloys (Fig. 1), it becomes apparent that the initial region in which magnesium has little effect on hydrogen absorption by cerium is associated with the formation of solid solutions of magnesium in cerium. Alloys with compositions approximating  $MgCe$  (14.79 wt. % Mg) have the greatest effect on absorption. Peritectic reactions forming the compounds  $MgCe$  from  $Mg_2Ce$  (27.77% Mg) and  $Mg_2Ce$  from  $Mg_3Ce$  decrease hydrogen absorption by the alloys. To an even greater extent, this relates to alloys richer in magnesium, which do not absorb hydrogen at room temperature, either in their original state or after heat treatment.

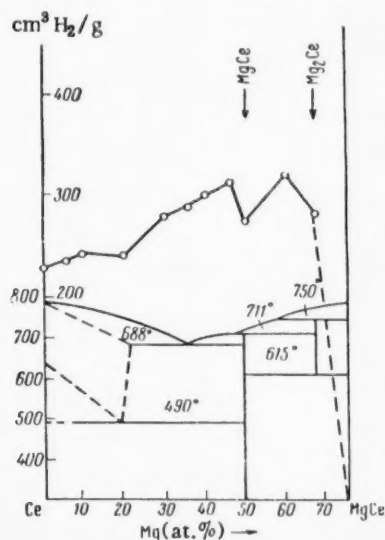


Fig. 1. Amount of hydrogen absorbed (cc/g) by cerium-magnesium alloys.

The cerium hydride  $CeH_3$  is air hypergolic and reacts vigorously with water liberating hydrogen [2-4]. According to the literature [5,6], magnesium hydride is not very sensitive to air and moisture. Cerium-magnesium alloys containing up to 5 atm % Mg and hydrogenated to saturation behave like cerium hydride, but with 10 atm % Mg and more the hydrogenation products are air hypergolic only when vigorously ground, and above 30 atm % Mg they do not react at all with air and moisture.

Thermal decomposition of the hydrogenation products, like that of the cerium hydride  $CeH_3$ , evolves hydrogen in several stages. For example, with the alloy containing 46 atm % Mg vigorous hydrogen evolution was observed in the interval 350-420°, and approximately  $\frac{2}{5}$  of the total hydrogen was evolved; the second stage of hydrogen evolution corresponded to the temperature interval 900-1050°C.

This work is interesting as an indication of the possibility of hydrogenating cerium-magnesium alloys to  $Mg_mH_{2m}Ce_nH_{3n}$  mixtures, the composition of which in the limiting case is given by  $MgCeH_5$ . The nature of the hydrogenation of binary alloys of cerium and magnesium is distinct from that of pure cerium and magnesium, and the properties of the resulting "double hydrides" are distinct from the properties of each of the simple hydrides  $CeH_3$  and  $MgH_2$ . For example, metallic magnesium is completely inactive toward hydrogen at room temperature, metallic cerium readily absorbs hydrogen, while cerium-magnesium alloys are completely hydrogenated at room temperature, although significantly more slowly than is pure cerium. With an increase in the magnesium content of the alloy, the air hypergolicity of the hydrogenation product—a property characteristic of cerium hydride—decreases gradually, and the stability with respect to water—a property characteristic of magnesium hydride—increases.

Thus, these products of the complete hydrogenation of cerium-magnesium alloys, which have approximately the composition  $MgH_2CeH_3$  or  $MgCeH_5$ , have properties which occupy a position intermediate to those of the simple hydrides  $CeH_3$  and  $MgH_2$  composing them.

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## OXIDATION OF DIISOPROPYLMERCURY

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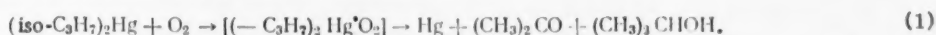
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pp. 107-109, November, 1961

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The oxidation of dicyclohexylmercury (DCHM) in various solvents was investigated in previously reported work [1]. The question naturally arises as to whether other organomercury compounds with secondary radicals also react with oxygen. With the aim of answering this question, we investigated the simplest member of this class—diisopropylmercury (DIPM). According to the literature [2], DIPM is a colorless liquid boiling at 119-121°/125 mm. This compound liberates mercury when stored in air. We propose that the reason for this is the action of oxygen, as was established in the case of DCHM. As a matter of fact, DIPM readily undergoes oxidation by atmospheric oxygen under ordinary conditions.

In the present work, we studied certain processes in the oxidation of DIPM in isopropyl alcohol, carbon tetrachloride, and chloroform. When oxidation was carried out in isopropyl alcohol, mercury was liberated and a significant amount of acetone was obtained. In addition, the presence of isopropyl alcohol in the oxidation products would be expected. In the present case, the formation of isopropyl alcohol could be detected only by the use of a labeled compound.

Labeled isopropyl alcohol was indeed observed in the reaction products when  $C^{14}$ -DIPM was used. Thus, the process can be represented in general form by means of the equation:



Significantly more acetone plus alcohol was formed than would correspond to the above equation. This discrepancy can be explained by oxidation of the solvent— isopropyl alcohol—to acetone. A similar phenomenon was previously noted during oxidation of DCHM. Our present experiments actually confirm oxidation of the solvent. Thus, in the oxidation of  $C^{14}$ -DIPM in isopropyl alcohol (molar ratio of 1:28) at 65-66° for 11 hours, the activity of the acetone (4450 imp/minute) was only about 20% of the activity (22,400 imp/minute) of the original organomercury compound. The decreased activity of the acetone is explained by dilution with acetone formed by oxidation of the solvent, isopropyl alcohol. The isopropyl alcohol remaining after the reaction had an activity of 670 imp/minute.

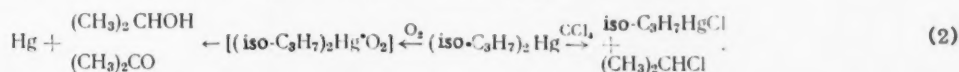
The amounts of alcohol and acetone formed from the  $C^{14}$ -DIPM were calculated from their relative activities. These values were, respectively, about 158 and 43 mole %, based on the mercury liberated.

The formation of acetone from the solvent was also confirmed by oxidation of DIPM in  $C^{14}$ -isopropyl alcohol (molar ratio of 1:23). The activity of the acetone (3040 imp/minute) comprised about 55% of the activity (5540 imp/minute) of the original alcohol when the reaction was carried out for 15 hours at 66-67°.

The amount of acetone formed by oxidation of the solvent varied from 150 to 400 mole %, depending on the experimental conditions.

The reaction was more complex in chlorine containing solvents,  $CCl_4$  and  $CHCl_3$ . The data showed that the solvent reacts with the DIPM with the formation of isopropylmercury chloride,  $\text{iso}-C_3H_7HgCl$  (about 70%) and, in the case of  $CCl_4$ , isopropyl chloride.

In these solvents, the reaction can be represented by the following general scheme:



On the one hand, the previously described oxidation of DIPM with the formation of Hg, alcohol, and acetone takes place, and on the other hand, the interaction of  $\text{CCl}_4$  (or  $\text{CHCl}_3$ ) with the organomercury compound occurs; the latter reaction is initiated by intermediate peroxide compounds. It is known from the literature [3] that acyl peroxides initiate the interaction of organomercury compounds with  $\text{CCl}_4$ . Predominance of one or the other course depends on the

TABLE 1. Oxidation of DIPM in  $\text{CCl}_4$  and  $\text{CHCl}_3$

Reaction product	Mole % with respect to DIPM		
	$\text{CCl}_4^*$	$\text{CCl}_4^{**}$	$\text{CHCl}_3^*$
Hg	14.3	0	28.6
iso- $\text{C}_3\text{H}_7\text{HgCl}_4$	71.4	85.7	71.2
$(\text{CH}_3)_2\text{CO}$	54.3	33.0	60.0
$(\text{CH}_3)_2\text{CHOH}$	11.4	0	28.6
$(\text{CH}_3)_2\text{CHCl}$	11.4	44.3	—

\*Reaction carried out for 20 hours at 17-20°. DIPM charged was 0.0035 mole in 0.09 mole of solvent.

\*\*Reaction carried out for 18 hours at 44°. DIPM charged was 0.007 mole in 0.09 mole of solvent.

connected to an oxygen burette by means of polyethylene tubing; the reaction mixture was agitated by a mechanical stirrer.

The oxidation of DIPM in isopropyl alcohol was carried out in an oxygen atmosphere in sealed tubes; agitation was accomplished by shaking the tubes.

The amount of acetone in the reaction products and its activity were by combustion of the 2,4-dinitrophenylhydrazones (m.p. 125°, from ethanol) and measurement of the activity with an internal counter.

The filtrate from the separation of the hydrazone was diluted with unlabeled acetone, which was subsequently precipitated with an excess of a hydrochloric acid solution of 2,4-dinitrophenylhydrazine. The filtrate was then distilled. The small, first fraction was collected, dried, and again distilled. The activity of the alcohol after the reaction was determined in this fraction.

The results of the oxidation of DIPM in  $\text{CCl}_4$  and in  $\text{CHCl}_3$  are presented in Table 1.

The reaction mixture was distilled under vacuum. The residue contained the mercury and isopropylmercury chloride; the latter was obtained as needles (from acetone) with an m.p. of 93-94°. Found %: Hg 71.38; Cl 12.73.  $\text{C}_3\text{H}_7\text{HgCl}$ . Calculated %: Hg 71.87; Cl 12.72.

The distillate fraction was quantitatively analyzed. Quantitative analysis for the isopropyl alcohol and the isopropyl chloride was carried out spectroscopically; the isopropyl alcohol was determined from the band at  $950\text{ cm}^{-1}$  in  $\text{CCl}_4$  and in  $\text{CHCl}_3$ , while the band at  $615\text{ cm}^{-1}$  was used for the isopropyl chloride.

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# SYNTHESIS AND SOME REACTIONS OF PYRIDYLETHYNYLCARBINOLS

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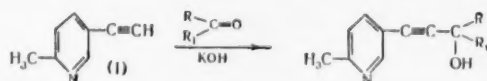
M. V. Lomonosov Moscow State University

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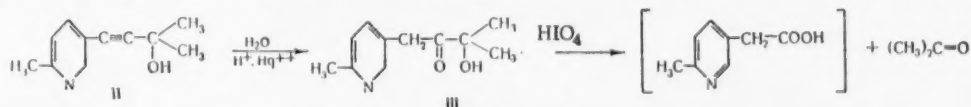
Original article submitted July 6, 1961

There has been very little study of heterocyclic bases having a triple bond in the side chain. Moreover, such compounds can serve as starting materials for the synthesis of an entire series of new systems.

In our study of the properties of an acetylenic group bonded to a pyridine ring, we carried out the condensation of 2-methyl-5-ethynylpyridine (I) [1] with aldehydes and ketones under the conditions of the Favorskii reaction. As in the case of other substituted acetylenes [2], the best yields were obtained with a four- to five-fold excess of the base. The condensation of I with ketones proceeds smoothly and with good yields in a medium of absolute ether at 0°. However, the reaction of I with aldehydes can be carried out only at a temperature of -20 to -40° and at high dilution in tetrahydrofuran as a solvent.

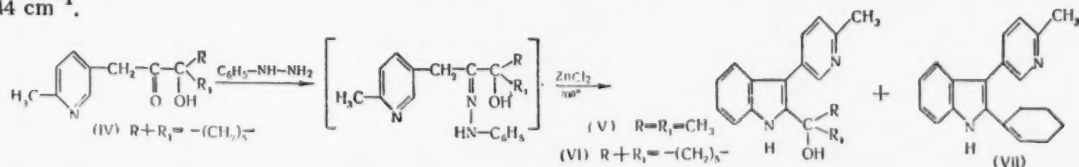


The resulting tertiary carbinols do not undergo the Kucherov reaction in 15-20% sulfuric acid. Only by using 25% sulfuric acid was it possible to convert carbinol II ( $R+R_1=CH_3$ ) to the corresponding  $\alpha$ -keto alcohol III, the structure of which was proved by infrared spectroscopy (presence of a band at  $1714\text{ cm}^{-1}$ , which is characteristic of a C=O group not conjugated with an aromatic ring) and by the separation of acetone (as the 2,4-dinitrophenylhydrazone) from the products of the periodate oxidation of the carbinol.

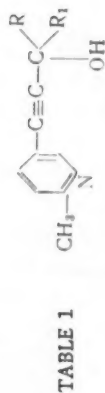


A Fischer reaction was carried out with hydroxyketone III by heating the phenylhydrazone with a catalytic amount of anhydrous zinc chloride at 190-210°. 2-(2-Hydroxyisopropyl)-3-(6-methyl-3-pyridyl) indole (V) was isolated as the sole reaction product. It was identified by infrared spectroscopy (presence of N-H- and OH vibrational frequencies in the  $3200\text{-cm}^{-1}$  region and the absence vibrational frequencies due to an unsaturated bond in the region of  $1640$  to  $1660\text{ cm}^{-1}$ ) and by ultraviolet spectroscopy (a maximum in the  $267\text{-m}\mu$  region, which is characteristic of  $\beta$ -phenylindoles).

When the analogous reaction was carried out with hydroxyketone IV, 2-(1-hydroxy-1-cyclohexyl)-3-(6-methyl-3-pyridyl) indole (VI) was obtained, and from its dehydration products was separated 2-(1-cyclohexenyl)-3-(6-methyl-3-pyridyl) indole (VII); the i.r. spectrum of the latter compound contained a vibrational frequency in the region of  $1644\text{ cm}^{-1}$ .







R	R <sub>1</sub>	Yield, %	M.p., °C	B.p., °C/mm	C, %		H, %		N, %	
					found	calculated	found	calculated	found	calculated
CH <sub>3</sub>	CH <sub>3</sub>	90	101—102	—	75.43 75.61	75.43	7.52 7.55	7.43	—	—
C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	80	98—99	—	75.98 75.79	76.19	7.94 8.15	7.94	—	—
C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	48	30—32	146—150°/2	76.53 76.26	76.85	8.46 8.47	8.37	—	—
(CH <sub>3</sub> ) <sub>3</sub> C	CH <sub>3</sub>	70	100—101	—	77.52 77.73	77.45	9.22 9.31	9.20	—	—
—(CH <sub>2</sub> ) <sub>5</sub> —		98	116—118		78.38 78.14	78.14	8.02 7.93	7.91	—	—
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	60	104—105		—	—	—	—	5.69 5.71	5.91
C <sub>2</sub> H <sub>5</sub>	H	38.7*	120—123**	165—167°/8	50.32 50.25	50.50**	4.31 4.08	3.99	—	—
C <sub>3</sub> H <sub>7</sub>	H	20.0*	103—104***	182—184°/8	—	—	—	—	9.46 9.43	9.09***
—C <sub>4</sub> H <sub>9</sub>	H	35.0*	112—114**	178—180°/6	52.37** 52.52	52.78	4.80 4.91	4.66	—	—

\* Based on the pyridylacetylene introduced.

\*\* Picrate.

\*\*\* Phenylurethan.

## EXPERIMENTAL

**Condensation of I with ketones.** To a mixture of 0.1 mole of I and 0.4 mole of powdered KOH in 25 ml of absolute ether at 0° was added, with stirring, 0.1 mole of the ketone. The mixture was allowed to stand overnight; it was then saturated with carbon dioxide, and the carbinol was separated (see Table 1).

**Condensation of I with aldehydes.** A mixture of 0.05 mole of I and 0.25 mole of powdered KOH in 25 ml of absolute tetrahydrofuran was cooled to -25 to -40°, a solution of 0.1 mole of the aldehyde in 20 ml of absolute tetrahydrofuran was added slowly (over a period of 1.5-2 hours) and with stirring, and stirring was continued for an additional 2 hours. On the following day, the mixture was acidified and extracted with ether; the aqueous solution was neutralized, extracted with ether, and the residue remaining after evaporation of the solvent was chromatographed on aluminum oxide. The I was eluted with petroleum ether, and the carbinol was eluted with a mixture of benzene and acetone (1:1).

**2-Methyl-5-(3-hydroxy-3-methyl-2-oxobutyl)pyridine (III).** A solution of 8.7 g of 2-methyl-5-(3-methyl-3-hydroxy-1-butyryl)pyridine (II,  $R=R_1=CH_3$ ) in 50 ml of 25% sulfuric acid was refluxed for 10 hours in the presence of 0.1 g of mercuric oxide. The reaction mixture was then neutralized with sodium carbonate and extracted with chloroform. After evaporation of the solvent, the residue was distilled under vacuum. The yield was 50.5%, b.p., 158-162°/7 mm; m.p., 52-54°. Found %: N 6.95, 7.05.  $C_{11}H_{15}O_2N$ . Calculated %: N 7.25.

**2-(2-Hydroxyisopropyl)-3-(6-methyl-3-pyridyl)indole (V).** A mixture of 1.9 g of III and 1 g of phenylhydrazine was heated (150°) for 0.5 hour; 0.2 g of anhydrous zinc chloride was then added, and heating was continued for another 1.5 hours at 200-220°. The reaction mixture was cooled and twice reprecipitated from acid solution. The yield was 0.5 g (19%); m.p. 150-152° (from a 1:1 mixture of benzene and petroleum ether).  $\lambda_{max}^{267 m\mu}$  ( $\log \epsilon$ , 4.08) (from methanol). Found %: N 10.92, 10.81.  $C_{17}H_{19}ON_2$ . Calculated %: N 10.53.

**2-Methyl-5-(2-(1-hydroxy-1-cyclohexyl)-2-oxoethyl)pyridine (IV).** A solution of 4.3 g of II ( $R+R_1=-(CH_2)_5$ ) in 25 ml of 25% sulfuric acid was refluxed for 7 hours in the presence of 0.05 g of mercuric oxide, and the mixture was then neutralized with sodium carbonate and extracted with benzene. The extract was evaporated and chromatographed on aluminum oxide. There was obtained 2.7 g (49%) of a substance with an m.p. of 64-65°. Found %: N 6.51, 6.15.  $C_{14}H_{19}O_2N$ . Calculated %: N 6.00.

**2-(1-Hydroxy-1-cyclohexyl)-3-(6-methyl-3-pyridyl)indole (V).** A mixture of 5.8 g of IV and 2.7 g of phenylhydrazine was heated (150°) for 0.5 hour; 0.2 g of anhydrous zinc chloride was then added, and heating was continued for an additional 2.5 hours at 175-190°. The mixture was cooled, twice reprecipitated from acid solution, and the resulting oil was extracted with benzene. From the extract was obtained 0.9 g (12%) of V with an m.p. of 152-154°;  $\lambda_{max}^{275 m\mu}$  ( $\log \epsilon$ , 4.01) (from methanol). Found %: 9.03, 8.98.  $C_{20}H_{22}ON_2$ . Calculated %: N 9.11.

The benzene-insoluble residue was chromatographed on aluminum oxide. There was obtained 0.3 g of VI; m.p. 70-71°. Found %: N 9.46, 9.33.  $C_{20}H_{20}N_2$ . Calculated %: N 9.72.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

# DOUBLE OXIDES IN THE SYSTEM URANIUM - TUNGSTEN - OXYGEN

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Up to the present, there has been no investigation of double oxides of uranium and tungsten. The literature contains merely some reference to the preparation of hydrated uranyl tungstates and polytungstates [1-3].

We have studied the oxides formed by the interaction of various uranium and tungsten oxides and also oxides formed during thermal decomposition and hydrogen reduction of uranyl tungstate. The starting materials for the preparations were analytical grade tungstic acid and uranyl nitrate; the remaining materials ( $WO_2$ , W,  $UO_2$ ,  $U_3O_8$ , and  $UO_3$ ) were obtained from these two compounds. The methods used in the preparations are generally known. The investigation was carried out by x-ray phase analysis RKD-57 camera; Cu  $K_{\alpha}$  radiation; Ni filter). A series of samples were photographed with monochromatic Cu  $K_{\alpha}$  radiation produced by reflection from a face of germanium single crystal (this gave the best resolution of the lines for the camera diameter used) [4]. Samples in the  $UO_3$ - $WO_3$  system were prepared by boiling aqueous suspensions of  $H_2WO_4$  and  $UO_2(OH)_2$  for a prolonged period, then evaporating the suspension to dryness, and calcining at  $900^\circ$  for 45 hours. X-ray phase analysis of the resulting samples showed that only one compound— $UO_2WO_4$ —is formed in the  $UO_3$ - $WO_3$  system (see Table 1). Uranyl chromate and molybdate were synthesized for purposes of comparison. Uranyl chromate was prepared by dehydration of  $UO_2CrO_4 \cdot 5.5 H_2O$  at  $400^\circ$ ; the molybdate was prepared by sintering  $U_3O_8$  with an excess of  $MoO_3$  in air at  $750^\circ$ .

TABLE 1. X-ray Phase Analysis Results

Composition of starting material	Method of preparation	Phases observed
$UO_3 : WO_3 = 1 : 1$	Annealing, $900^\circ$	$UO_2WO_4$
$UO_3 : WO_3 = 1 : 2; 1 : 3$	Annealing, $900^\circ$	$UO_2WO_4 + WO_3$
$UO_3 : WO_3 = 3 : 1$	Annealing, $450^\circ$	$UO_{3-x} + WO_3$
$UO_2WO_4$	$H_2$ , $300^\circ$	$UO_2WO_4$
Same	$H_2$ , $400^\circ$	Same
"	$H_2$ , $500^\circ$	$WO_2UO_2$ , $UWO_{5+x}$
"	$H_2$ , $600^\circ$	W, $UO_2$ , $WO_2$
"	$H_2$ , $700^\circ$	W, $UO_2$
$UO_2 : WO_2 = 1 : 1; 2 : 1; 1 : 2$	Annealing, $1250^\circ$	$WO_2$ , $UO_2$
$UO_2WO_4 : W = 1 : 1$	Annealing, $1250^\circ$	$WO_2$ , $UO_2$
$U_3O_8 : W = 1 : 1$	Annealing, $1250^\circ$	Same
$U_3O_8 : WO_2 = 1 : 1$	Annealing, $1250^\circ$	$UO_2$ , $(U,W)O_{3-x}$
$U_3O_8 : WO_3 = 1 : 1$	Annealing, $1250^\circ$	$U_3O_8$ , $(U,W)O_{3-x}$
$UO_2 : WO_3 = 1 : 1; 1 : 10$	Annealing, $900^\circ$	$(U,W)O_{2+y}$ , $(U,W)O_{3-x}$
$UO_2 : WO_3 = 1 : 25; 1 : 50$	Annealing, $900^\circ$	$(U,W)O_{3-x}$
$UO_2WO_4$	Vacuum decomp., $800^\circ$	$UWO_{5.5}$
$UO_2WO_4$	Vacuum decomp., $900^\circ$	$UWO_{5.01}$
$U_3O_8 + UO_2 + 2WO_2 + 2WO_3$	Annealing, $900^\circ$	$(U,W)O_{3-x}$ , $(U,W)O_{2+y}$
$UWO_{5.01}$	Annealing, $1250^\circ$	$(U,W)O_{5+x}$ , $UO_2$ , $(U,W)O_{3-x}$

The x-ray photographs of all three substances were closely similar (Fig. 1), which indicates that they are isostructural.

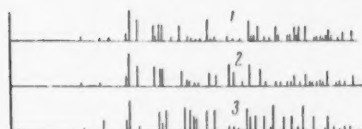


Fig. 1. Schematic of Debye photographs of  $\text{UO}_2\text{WO}_4$  (1),  $\text{UO}_2\text{MoO}_4$  (2), and  $\text{UO}_2\text{CrO}_4$  (3).

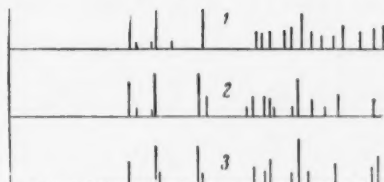


Fig. 2. Schematic of Debye photographs of  $\text{U}_3\text{O}_8$  (3),  $\text{UWO}_{5+x}$  phase (1), and  $\text{UMoO}_{5+x}$  (2).

Oxides of uranium and tungsten in lower valence states were prepared by thermal decomposition of  $\text{UO}_2\text{WO}_4$  under vacuum at 600-900°, by reduction of uranyl tungstate with hydrogen at temperatures of 300-800, and by sintering different uranium and tungsten oxides in evacuated ampoules at 1250° and 900°. The results of phase analyses of these products are presented in Table 1. It is apparent from these data that two new phases appeared in the case of the lower oxides of uranium and tungsten. One of these phases was structurally close to  $\text{U}_3\text{O}_8$  (Fig. 2). The composition of the phase structurally close to  $\text{U}_3\text{O}_8$  corresponds to the formula  $\text{UWO}_{5+x}$ . As similar phase was formed during decomposition of  $\text{UO}_2\text{MoO}_4$ . The x-ray photograph of this phase was identical to that of the  $\text{UWO}_{5+x}$  phase. The  $\text{UWO}_{5+x}$  phase was obtained in its purest form by thermal decomposition of  $\text{UO}_2\text{WO}_4$  under vacuum at temperatures of 800 and 900°. The gross composition of this phase corresponds to the formula  $\text{UWO}_{5.5}$  for the sample prepared at 900°. The Debye photograph of the other phase was indexed in the cubic system with a primitive unit cell parameter of  $a = 3.805 \pm 0.001$  kX.

A compound with a cubic unit cell was synthesized by sintering  $\text{UO}_2$  and  $\text{WO}_3$  in ratios of 1:1 and 1:10. At  $\text{UO}_2$ -to- $\text{WO}_3$  ratios of 1:25 and 1:50, tetragonal distortion of the primitive unit cell occurred. Furthermore, when  $\text{WO}_3$  and  $\text{WO}_2$  were sintered in ratios of 15:1, 25:1, and 50:1 and also when  $\text{WO}_3$  and  $\text{ThO}_2$  were sintered in a ratio of 10:1, a cubic phase was not observed, and rhombic distortion of the cubic unit cell occurred, just as in the case of  $\text{WO}_3$ . Thus, a cubic phase is formed only in the presence of uranium; this phase is structurally close to  $\text{WO}_3$  and apparently contains a smaller amount of oxygen, i.e., its composition is expressed by the formula  $(\text{W,U})\text{O}_{3-x}$ . A phase of the  $\text{UO}_2$  was present in the  $\text{UO}_2 + 10\text{WO}_3$  sample. This phase probably contained a certain amount of tungsten, since the lattice parameter of this phase ( $a = 5.461 \pm 0.001$  kX) differed from the lattice periods of the  $\text{UO}_{2+x}$  phases, although insignificantly. A cubic phase was not formed in the  $\text{UO}_2 + 25\text{WO}_3$  sample. It can be concluded from this that the ratio of U to W in the cubic phase is close to 1:15-20, and  $x$  is about 1/15 to 1/20.

Thus, the  $\text{UWO}_5$  samples had different phase compositions depending on the method of preparation: the products obtained by reduction and by thermal decomposition of uranyl tungstate contained a  $\text{UWO}_{5+x}$  phase, while sintering of the oxides gave a mixture of  $(\text{U,W})\text{O}_{3-x}$  and  $\text{UO}_2$  or  $(\text{U,W})\text{O}_{2+y}$  phases. Three phases were found in the sample after sintering  $\text{UWO}_{5+x}$  at 1250°: the initial oxide  $\text{UWO}_{5+x}$ ,  $\text{UO}_{2+x}$  and  $(\text{U,W})\text{O}_{2+y}$  and  $(\text{U,W})\text{O}_{3-x}$ ; i.e., the  $\text{UWO}_{5+x}$  phase disproportionates at the higher temperature.

No interaction between  $\text{UO}_2$  and  $\text{WO}_2$  was observed up to 1250°. The lattice parameters of the initial phase did not change during sintering; i.e., solid solutions were apparently not formed.

In conclusion, we express our deep appreciation to Yu. P. Simanov for a series of valuable discussions.

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# A COMPARATIVE STUDY OF THE KINETICS OF THE CONVERSION OF VARIOUS HYDROCARBONS TO ACETYLENE IN AN ELECTRICAL DISCHARGE IN A STATIC SYSTEM

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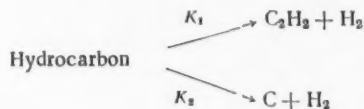
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There have been numerous earlier studies of electrocracking of methane to acetylene.\* It has been shown that this method is applicable to the synthesis of acetylene. As regards methane homologs and olefins, their conversion has mainly been carried out in low-temperature discharges (silent and glow discharges). Under these conditions, either acetylene is not formed at all, or its formation is associated with high energy consumption, or else a mixture of hydrocarbons is subjected to cracking [4]. Thus, the literature contains almost no data which permit a comparison between the kinetics and the energetics of electrocracking of different hydrocarbons. The present communication is devoted to this question.

## EXPERIMENTAL

**Method.** The process was carried out under static conditions with a high-voltage glow and, chiefly, arc discharge at pressures of 35 and 70 mm Hg, currents of 100 and 300 ma, and distances between electrodes of 15 and 50 mm. The basis of the apparatus consisted of a reactor (a five-liter flask) with two internally water-cooled, brass electrodes. Details of the method have been described previously [1]. At the conclusion of an experiment, a sample of the gas was collected with a mercury pump and analyzed for:  $C_2H_2$  with an alkaline solution of mercuric cyanide,  $C_2H_4$  with 67% sulfuric acid activated with silver oxide, and  $C_3H_6$  with 87% sulfuric acid.

The hydrogen was burned over copper oxide at 250°. The methane, ethane, and propane were determined in the residue remaining from the hydrogen combustion. The kinetic calculations took into account two main courses of the reaction:



The over-all rate constant for hydrocarbon decomposition was determined with a first order equation:

$$K_1 + K_2 = \frac{1}{\tau} \ln \frac{1}{1-\Delta},$$

where  $\Delta$  is the over-all hydrocarbon conversion and is equal to the ratio of the amount of hydrocarbon decomposed to the initial amount.

Figure 1 presents the change in the concentration of acetylene in the products from the conversion of methane and of ethylene as a function of discharge time (curves 1 and 2) and as a function of energy consumption in kilowatt-hours per cubic meter of acetylene, reduced to standard conditions (curves 3 and 4). The experimental conditions were: reactor volume, 5 liters; initial pressure, 70 mm Hg; current, 100 ma; distance between electrodes, 50 mm.

It is apparent that an accumulation of acetylene occurs initially, but at longer reaction times there is a decrease in the concentration of  $C_2H_2$  owing to decomposition of the acetylene to the elements. Curves of the same

\*A detailed bibliography may be found in reference [1]. See also references [2,3].



nature were also obtained under other experimental conditions and also with homologs of methane and ethylene; there was, however, this difference: there was a change in the maximum concentration and also in the reaction time corresponding to this maximum.

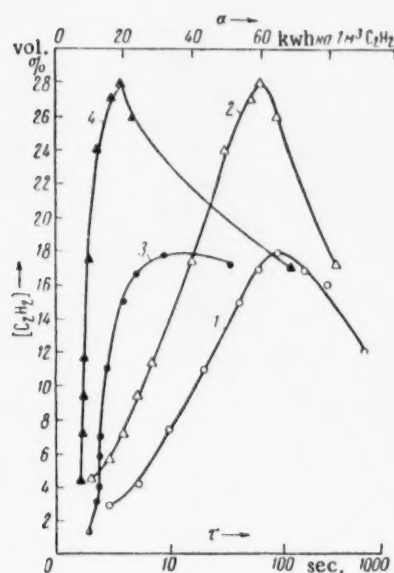


Fig. 1. Dependence of acetylene concentration during methane and ethylene cracking on discharge time (1 and 2) and on energy consumption per unit volume of acetylene (kwh per cu. m. of  $C_2H_2$ ) (3 and 4). 1,3)Methane; 2,4) ethylene.

propylene. If the energy consumption during commercial production of acetylene by the carbide process is taken as 12 kwh/cu. m., the advantage of electrocracking becomes obvious, particularly since the transition to large-scale, flow-type equipment would permit still greater economies in current consumption.

Table 2 also presents values of the thermochemical coefficient of discharge efficiency ( $\eta$ ), which amounts to an evaluation of the part of the discharge energy thermochemically required for the production of a given amount of acetylene. A high value of the thermochemical c.d.e., up to 0.4-0.5, distinguishes electrocracking of hydrocarbons from other endothermic discharge reactions. This can be explained on the assumption of a chain mechanism for the electrocracking reaction by analogy to thermal cracking, for which chain kinetics may be considered proved. It can be assumed that only the initial stage of the reaction, specifically the formation of radicals and atoms, takes place in this case under electron impact. Further development of the chain is accomplished by thermal activation of the individual links.

Inspection of the over-all rate constants for hydrocarbon decomposition (Table 1) reveals that they are all close to the same value under equivalent experimental conditions. However, the sum  $K_1 + K_2$  increases during the transition to higher currents and also with an increase in the distance between electrodes. In other words, with the transition to a more powerful discharge, the tendency of the hydrocarbons to crack increases, and to an equal extent for all hydrocarbons.

If the initial cracking rate is expressed by  $(K_1 + K_2) P_i$  (on the assumption of first order kinetics), where  $P_i$  is the initial hydrocarbon pressure, and if this rate is referred to unit power, the resulting value, or "discharge energy efficiency" [4],\* remains approximately constant for all of the hydrocarbons regardless of experimental conditions (Table 1). The individual deviations are irregular and apparently are due to accidental causes. This important re-

\*Further details on energy efficiency are given in references [3,5].

Table 1 presents the basic indices of the process for various experimental conditions.

A comparison of the actual acetylene concentration with that theoretically possible indicates that the major course of the reaction under the conditions indicated is cracking to acetylene. Ethylene comprised only 10-15% of the acetylene content. Decomposition of the hydrocarbon to the elements is a side reaction which increased from methane to propane and further, and to a greater extent, to propylene, i.e., to hydrocarbons less rich in hydrogen. The acetylene concentrations obtained with these hydrocarbons significantly exceeded the maximum concentration obtained by methane cracking (by a factor of 1.5 in the case of propylene, for example). It is very fundamental that maximum concentrations corresponded to considerable consumption of the original hydrocarbon (the depth of cracking was 80%, on the average).

Another very important index of electrocracking is the energy consumption per cu.m. of  $C_2H_2$  ( $\alpha$ ). The change in energy consumption with acetylene concentration can be traced for methane and ethylene cracking under specific conditions by means of Curves 3 and 4 of Fig. 1. It is apparent that the change in energy consumption is small during the initial period of acetylene accumulation. The nature of the curves was the same for the other hydrocarbons studied and for other experimental conditions. Energy consumptions for the initial reaction period are presented in Table 2. It is apparent that the energy consumption was comparatively small for all of these hydrocarbons; it was a maximum for methane, decreased substantially for ethane and propane, and to still greater extent for ethylene and propylene.

sult can be interpreted to mean that the rate of conversion of hydrocarbons in a glowing arc does not depend on the structure of the hydrocarbon, but does depend on the energy supplied to the discharge.

TABLE 1. Fundamental Indices of the Electrocracking of Methane, Ethane, Propane, Ethylene, and Propylene under Various Discharge Conditions

Hydro- carbon	Distance between electrodes, mm							
	15				50			
	Current, ma							
	100		300		100		300	
	Pressure, mm Hg							
	37	70	35	70	35	70	35	70

Maximum  $C_2H_2$  concentration, vol. %

$CH_4$	17,8	18,2	20,2	19,0	17,4	17,8	19,0	16,2
$C_2H_6$	—	—	24,4	19,4	23,2	21,2	20,4	19,4
$C_3H_8$	26,6	22,6	24,2	20,8	23,8	20,6	22,0	18,4
$C_2H_4$	28,4	27,4	29,2	24,6	30,2	27,6	27,8	24,0
$C_3H_6$	30,8	26,8	28,2	23,0	28,2	25,4	25,0	19,8

Total cracking, per cent of corresponding maximum concentration

$CH_4$	85	96	95	94	95	93	90	88
$C_2H_6$	—	—	90	75	91	80	83	75
$C_3H_8$	85	73	80	76	80	87	70	68
$C_2H_4$	85	87	80	75	86	82	82	75
$C_3H_6$	90	85	85	82	86	83	80	70

Over-all (average) rate constant ( $K_1+K_2$ ) ( $sec^{-1} \cdot 10^4$ ) for hydrocarbon decomposition

$CH_4$	57	72	166	140	258	302	845	702
$C_2H_6$	84	69	207	114	412	279	1000	535
$C_3H_8$	99	85	157	115	355	207	585	538
$C_2H_4$	135	94	251	131	535	322	1050	700
$C_3H_6$	120	72	216	135	422	307	830	536

Discharge energy efficiency  $\varphi = \frac{(K_1+K_2)P_i}{W}$

$CH_4$	5	8	6	7	8	12	10	11
$C_2H_6$	6	7	6	6	10	10	10	8
$C_3H_8$	6	8	5	5	8	7	7	7
$C_2H_4$	7	9	6	5	12	11	10	7
$C_3H_6$	7	8	5	—	9	9	6	6

TABLE 2

Hydrocarbon	Energy consumption, kwh per cu. m.		Thermal effect, in kwh per cu. m. $C_2H_2$ , for the reaction: hydrocarbon $\rightarrow C_2H_2 + H_2$	Thermochemical coeff. of discharge eff. ( $\eta$ )
$CH_4$	9.6	12.7	4.7	0.27
$C_2H_6$	5.8	8.2	3.8	0.47
$C_3H_8$	6.6	9.4	3.7	0.38
$C_2H_4$	3.5	4.8	2.2	0.45
$C_3H_6$	4.6	6.4	2.7	0.41

In conclusion, we note that our data indicate the possibility of using the technological scheme developed for methane cracking for electrocracking of the other hydrocarbons studied in this work. Such application would be expected to possess advantages over methane cracking with respect to acetylene yield and with respect to reduction in energy consumption.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# APPLICATION OF THE TAFT EQUATION TO HYDRIDE TRANSFER IN AN ACID MEDIUM

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(Presented by Academician V. N. Kondrat'ev, May 31, 1961)

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The literature of recent years has exemplified the considerable interest in the Hammett equation as a basis for

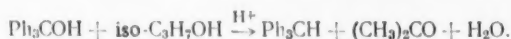
$$\lg k = \lg k_0 + \rho\sigma \quad (1)$$

establishing the connection between the structures of compounds and their reactivity. This has been promoted to a significant extent by the investigations of Taft [1] and Jaffe [2], who were able to extend substantially the region of applications of relationships of the type of (1) to polynuclear aromatic compounds with several substituents in the ring, on the one hand, and to aliphatic compounds, on the other. It is now possible to take into account the effect of polar coupling of a substituent with the reaction center ( $\sigma^+$ ) [3]. The latter is very important in reactions in which aromatic carbonium ions take part. These new possibilities have stimulated the publication of a large number of papers on the application of the Hammett-Taft relationship to reactions of various types, frequently without taking into account that these relationships have meaning only when applied to simple reactions. In the case of complex reactions of unknown mechanism, whether or not there is a linear relationship between the logarithm of the observed rate constant and  $\sigma$  (or  $\sigma^+$ ) provides no basis for far-reaching conclusions as to the nature of the process.

A required condition for the literal application of the Hammett-Taft rule to a complex reaction is a knowledge of the mechanism of this reaction; the rule can be applied to the rate constants and the equilibrium constants of the individual stages.

The correctness of this assertion will be shown below through an application of the Taft relationship to the reduction of four triarylcarbinols (TAC) with isopropyl alcohol by hydride transfer in an acid medium. It should be noted that only one paper [8] has appeared on the application of Eq. (1) to hydride transfer reactions.

As a result of a detailed study of the kinetics of the reduction by isopropyl alcohol in sulfuric acid medium of triphenylcarbinol (TPC) and its derivatives, diphenyl-*m*-tolylcarbinol (DPTK), di-*p*-tolylphenylcarbinol (DTPC), and di-*p*-anisylphenylcarbinol (DAPC), we previously obtained values of the effective rate constants over a temperature range from 35 to 90° and  $H_2SO_4$  concentrations from 4 to 60% [4-6]. As we have already shown [7], these reactions proceed by transfer of a hydride ion from the alcohol to the carbinol in accordance with the overall equation:



The value of the effective rate constant,  $k_{ef}$ , for hydride transfer depends on the acid concentration. The relationship is of a type which has extremums [4,5].

Figure 1 shows the relationship between  $\log k_{ef}$  and acid concentration for four carbinols. Since experimental values of  $k_{ef}$  were not obtained for all of the carbinols over the entire range of  $H_2SO_4$  concentration, Fig. 1 shows values of the constant calculated by means of Eq. (2). Just a glance at Fig. 1 makes it apparent that the course of

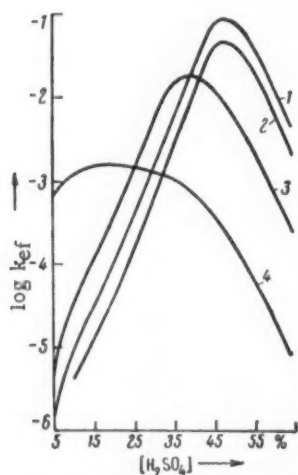


Fig. 1. Dependence of  $\log k_{ef}$  on  $H_2SO_4$  concentration at 90° for the carbinols: 1) TPC, 2) DPTK, 3) DTPC, 4) DAPC.

the change in the effective rate constants for the four carbinols depends on the  $\text{H}_2\text{SO}_4$  concentration at which the comparison of  $k_{\text{ef}}$  is carried out.

TABLE 1. Values of  $k_{\text{ef}}^{\circ} \cdot 10^3$  (liters/mole/second) at 90°

Substituents	$\sigma^+$	30% $\text{H}_2\text{SO}_4$	38% $\text{H}_2\text{SO}_4$	56% $\text{H}_2\text{SO}_4$
H(TPC)	0	1.53	11.60	36.60
m- $\text{CH}_3$ (DPTC)	0.066	0.72	6.72	18.15
p- $\text{CH}_3$ (DTPC)	-0.311	5.24	19.05	2.02
p- $\text{OCH}_3$ (DAPC)	-0.778	1.31	0.91	0.065

\* Values of the constants were calculated by Eq. (2).

We present a quantitative comparison of values of  $k_{\text{ef}}$  with the values of  $\sigma^+$ , which take into account direct polar coupling of the substituent with the reaction center [3]. As an example, Table 1 presents values of  $k_{\text{ef}}$  for three randomly selected concentrations of sulfuric acid, 30%, 38%, and 56%. The values of  $\sigma^+$  for the triarylcarbinols were calculated by a summation formula of the type proposed by Jaffe [2]:  $\sigma^+ = \sum \sigma_i^+$ , where  $\sigma_i^+$  is the value for the individual arene ring, which, in turn, was calculated as the sum of  $\sigma^+$  for the separate substituents on the ring.

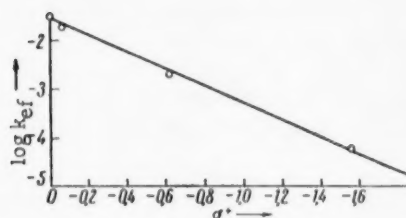
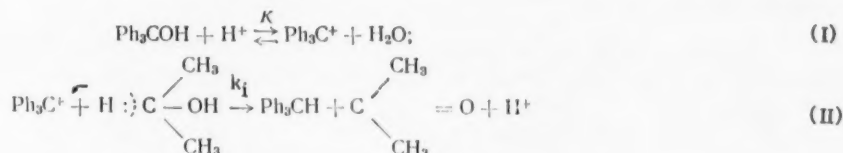


Fig. 2. Dependence of  $\log k_{\text{ef}}$  on the substituent constant  $\sigma^+$  at 90° and  $\text{C}_6\text{H}_5\text{SO}_4 = 56\%$ .

Figure 2 presents the data of Table 1 with  $\log k_{\text{ef}}$  plotted as a function of  $\sigma^+$ , where  $k_{\text{ef}}$  is the rate constant for the reduction of the corresponding TAC. It is apparent from Fig. 2 that a relationship of the type of (1) is followed for 56%  $\text{H}_2\text{SO}_4$ .  $\rho$  is determined to be +1.71 from the slope of the line. There was no correlation between  $\log k_{\text{ef}}$  and  $\sigma^+$  at the other two concentrations of  $\text{H}_2\text{SO}_4$ . As is apparent from these examples, neither the presence of a correlation between  $k_{\text{ef}}$  and  $\sigma^+$  in one example nor the absence of such correlation in the others can provide a basis for conclusions regarding the dependence of the reactivity of the triarylcarbinols on the nature of the substituents. Evidently, such must always be the case in the application of the Taft-Hammett relationship to observed rate constants of complex processes, such as the reduction of TAC by alcohols in acid media.

It has previously been shown [4,5] that the reduction of TAC by iso- $\text{C}_3\text{H}_7\text{OH}$  in acid medium is a complex process occurring in two steps:



where step (I) the equilibrium ionization of TAC to a carbonium ion, is the fast stage, and step (II), the transfer of a hydride ion from the alcohol to the carbonium ion, is the rate-limiting stage.

TABLE 2. Values of the Equilibrium Constant K for TPC and its Derivatives at 20°.

Substituent	H(TPC)	m- $\text{CH}_3$ (DPTC)	p- $\text{CH}_3$ (DTPC)	p- $\text{OCH}_3$ (DAPC)	$\rho_1$
K	$3.47 \cdot 10^{-7}$	$5.78 \cdot 10^{-7}$	$1.74 \cdot 10^{-5}$	$4.9 \cdot 10^{-2}$	
$\sigma^+$	0	-0.066	-0.311	-0.778	-3.25



It is not difficult to show that the observed rate constant for the decrease in TAC carbonium ion concentration is given by [4,5]

$$k_{ef} = k_e \left( \frac{Kc_0}{1 + Kc_0} \right) \left( \frac{1}{1 + K_{ROH}h_0} \right), \quad (2)$$

where  $k_e$  is the true rate constant of the limiting step (II),  $K$  and  $K_{ROH}$  are equilibrium constants for ionization of the carbinol and the alcohol, respectively, in acid medium, and  $c_0$  and  $h_0$  are the negative antilogarithms of the acidity functions of Deno and Hammett, respectively.

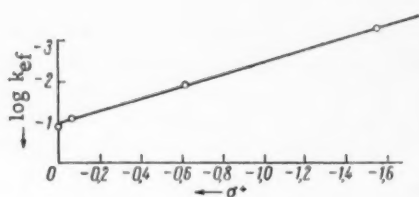


Fig. 3. Dependence of  $\log k_{ef}$  on  $\sigma^+$  at  $90^\circ$ .

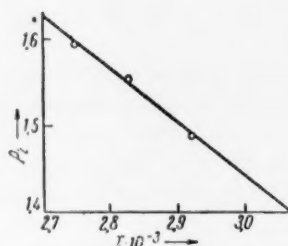


Fig. 4. Temperature dependence of  $\rho_2$ .

In comparing the reactivity of a carbinol in this reaction with the nature of the substituent, it is natural to compare the value of  $\sigma^+$ , which characterizes the substituent, with each of the constants appearing in Eq. (2), the true rate constant  $k_e$  and the equilibrium constant  $K$ .

By comparing  $\log K$  with the values of  $\sigma$  obtained by the different routes it was found that the data on the equilibrium constants also correlate with values of  $\sigma^+$ , i.e., the Taft equation is followed:

$$\lg K/K_0 = \rho\sigma^+. \quad (3)$$

Table 2 presents values of the equilibrium constant for carbinols with different substituents. The values of  $\sigma^+$  were taken from the work of Brown and Okamoto [3]. Practically the same values of  $\rho_1 = -3.25$  were obtained in the interval from 20 to  $80^\circ\text{C}$ .

It is also possible to show that Eq. (3) better describes the data on the ionization of nine other triarylcarbinols, presented in the paper by Deno and Schriesheim [9], than does the simple equation of Hammett. This gives  $\rho = -3.54$ , which is close to our value for  $\rho_1$ . There is little difference between these values and  $\rho = -3.97$  for the dissociation of triarylchloromethanes in liquid  $\text{SO}_2$  [2].

TABLE 3. Values of the True Rate Constant,  $k_t$  (liters/mole/second), for TPC and its Derivatives at Different Temperatures

Substituent	$70^\circ\text{C}$	$80^\circ\text{C}$	$90^\circ\text{C}$	$\sigma^+$
H(TPC)	128.8	335	912	0
m- $\text{CH}_3$ (DPTC)	80.0	188.4	451.9	-0.069
p- $\text{CH}_3$ (DTPC)	12.4	23.7	48.9	-0.311
p- $\text{OCH}_3$ (DAPC)	0.51	0.98	1.57	-0.778
$\rho_2$	+1.49	+1.56	+1.695	

It was found in this same manner that the Taft equation is also applicable to hydride ion transfer. Figure 3 presents an example of such a correlation for a temperature of  $90^\circ$ .

The data of Table 3 show that  $\rho_2$  increases with an increase in temperature, and the relationship  $\rho = a + b/T$  is followed, as shown in Fig. 4. The value of the characteristic temperature,  $b = 1.05^\circ \text{K}$ , is found from the slope of the line.

Using Eq. (3) to combine the values of  $\rho_1$  and  $\rho_2$  with equations of the type of (2), which may be written for any TAC and a standard substance (TPC), we obtain an expression for the logarithm of the ratio of the effective rate constants

$$\lg k_{\text{ef}}/k_{\text{ef}} = \rho_1\sigma^+ + \rho_2\sigma^+ + \lg \frac{1 + K_{0c_0}}{1 + K_{c_0}}. \quad (4)$$

It is apparent from Eq. (4) that whether  $k_{\text{ef}}$  obeys Eq. (1) depends on the value of the third term, which is a function of the absolute values of the basicity constant of the TAC and the acidity of the medium. Equation (1) will be followed in extreme cases. For example, when  $K_{0c_0} \ll 1$  and  $K_{c_0} \ll 1$ ,  $\lg k_{\text{ef}}/k_{\text{ef}_0} = \sigma^+(\rho_1 + \rho_2)$ , which can lead to a decrease of the constants in the  $\sigma^+$  series. In our case, this region is limited above by a sulfuric acid concentration of about 5%  $\text{H}_2\text{SO}_4$ . With  $K_{0c_0} \gg 1$  and  $K_{c_0} \gg 1$ ,  $\lg k_{\text{ef}}/k_{\text{ef}_0} = \rho_2\sigma^+$ . In the TAC series studied in the present work, this condition is fulfilled beginning with 46%  $\text{H}_2\text{SO}_4$ .

Equation (1) for  $k_{\text{ef}}$  will not be followed in the intermediate region.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# PYROLYSIS AND AND PHOTOLYSIS OF POLYFLUORONITROSOALKANES.

## THE REACTION OF NITROSO COMPOUNDS WITH NITRIC OXIDE

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N. F. Privezentseva, and L. L. Martynova

(Presented by Academician I. L. Knunyants and M. I. Kabachnik, June 1, 1961)

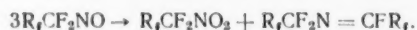
Translated from Doklady Akademii Nauk SSSR, Vol. 141, No. 1,

pp. 125-128, November, 1961

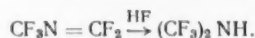
Original article submitted May 11, 1961

There has been little investigation of the pyrolytic and photolytic reactions of nitrosoalkanes, including polyhydrogenated derivatives. Trichloronitrosomethane decomposes when heated with the formation of trichloromethylcarbylamine dichloride [1]. Trifluoronitrosomethane is converted to trifluoronitro- and hexafluoroazoxymethane when heated in the presence of carbon [2]. N, N-bistrifluoromethylhydroxylamine nitrite has been separated from the products of the photochemical decomposition of trifluoronitrosomethane [2,3].

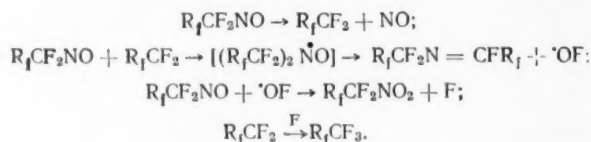
We have found that when polyfluoronitrosoethanes are heated at 100-150° (in a steel autoclave), they decompose by a single scheme with the formation of the corresponding nitroalkanes and azomethines as the major products:



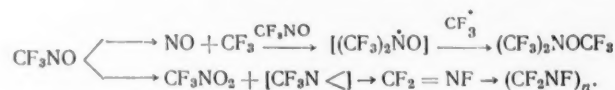
Properties of these newly synthesized compounds are presented in Table 1. Thermal decomposition of trifluoronitrosomethane under these conditions gave trifluoronitromethane (b.p. -32°), trifluoromethylcarbylamine difluoride (b.p. -32°), and bistrifluoromethylamine (b.p. -6°), which was formed by the addition of hydrogen fluoride (which was present due to the action of traces of moisture) to the carbylamine difluoride.



In addition to these compounds, tetrafluoromethane, difluorophosgene, and oxides of nitrogen were formed. The mechanism of the pyrolytic decomposition of polyfluoronitrosoalkanes can be expressed as a series of equations. The reactions include primary pyrolysis of the nitroso compound to  $R_f\cdot$  and NO radicals and their subsequent recombination:



Pyrolysis of trifluoronitrosomethane at 250-300° (in a flow-type apparatus at a contact time of 1-2 minutes) forms other products as a result of free-radical and oxidation-reduction reactions, which may be represented by the following schemes:



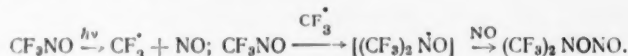
Fluorophosgene and fluoropicrin are also formed in this case, in conformity with the schemes presented above. Upon treatment with aniline, the perfluoroformine monomer, dimer, and polymer (which boiled up to 90-95°) formed the

TABLE 1. Properties of Newly Synthesized Compounds

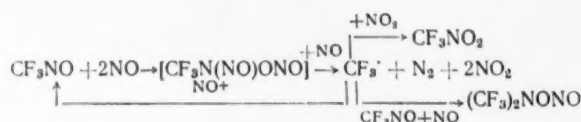
Compound	B.p., °C/mm	<sup>20</sup> <sub>d</sub> <sub>20</sub>	<sup>20</sup> <sub>n</sub> <sub>D</sub>	Found, %				Calculated, %			
				C	H	N	F	C	H	N	F
NO <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> N=CFCF <sub>2</sub> NO <sub>2</sub> <sup>1</sup>	52°/50	1,719	1,3520	16,81	—	14,54	45,28	—	16,70	—	46,4
ClCF <sub>2</sub> CF <sub>2</sub> N=CFCF <sub>2</sub> Cl	75	1,621	1,33	17,08	—	14,38	45,80	—	18,0	—	50,0
(CF <sub>3</sub> ) <sub>2</sub> NOCF <sub>3</sub>	+3,5	d <sub>4</sub> <sup>20</sup> 1,616	—	17,117	—	5,35	50,95	25,80	15,20	—	72,14
CF <sub>3</sub> =NF <sup>2</sup>	-36	—	—	17,94	—	6,17	51,10	24,02	—	—	—
(CF <sub>2</sub> =NF) <sub>2</sub> <sup>3</sup>	-6	—	—	15,19	—	6,70	71,68	—	14,48	—	68,67
CF <sub>3</sub> N(NO)ONO <sup>4</sup>	100(dec.)	—	—	15,20	—	16,22	64,13	—	14,48	—	68,67
CF <sub>3</sub> N(NO)ONa	m.p., 62°	—	—	14,40	—	15,87	66,90	—	14,48	—	68,67
CF <sub>3</sub> N(NO)OHNH(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	—	—	—	14,18	—	—	68,64	—	—	—	—
CF <sub>3</sub> N(NO)OHNH <sub>3</sub>	—	—	—	13,60	—	—	69,81	—	—	—	—
CF <sub>3</sub> N(NO)OHCH <sub>2</sub> Cl	—	—	—	8,65	—	18,02	37,70	—	7,9	—	37,5
CF <sub>3</sub> NHOCOC <sub>2</sub> H <sub>5</sub>	—	—	—	8,22	—	17,88	37,76	—	—	—	—
(C <sub>2</sub> H <sub>5</sub> NH) <sub>2</sub> C=NOCOC <sub>6</sub> H <sub>5</sub>	—	—	—	30,30	7,08	20,08	28,47	—	29,5	5,9	27,0
CF <sub>3</sub> N(NO)OHNH <sub>3</sub>	m.p., 86°	—	—	31,00	7,26	20,93	28,60	—	8,2	27	38,6
CF <sub>3</sub> N(NO)OHCH <sub>2</sub> Cl	—	—	—	8,60	3,70	28,00	38,59	—	5,25	—	24,8
CF <sub>3</sub> NHOCOC <sub>2</sub> H <sub>5</sub>	—	—	—	8,29	3,05	28,23	39,75	16,40	—	—	15,5
CF <sub>3</sub> NHOCOC <sub>2</sub> H <sub>5</sub>	m.p., 35°	—	—	6,71	—	11,95	22,55	16,90	—	—	—
CF <sub>3</sub> NHOCOC <sub>2</sub> H <sub>5</sub>	(in sealed capillary)	—	—	6,60	4,10	10,73	22,24	—	25,20	2,80	39,90
CF <sub>3</sub> NHOCOC <sub>2</sub> H <sub>5</sub>	m.p., 62°	—	—	25,74	4,38	8,97	39,81	—	47,0	2,90	28,0
(C <sub>2</sub> H <sub>5</sub> NH) <sub>2</sub> C=NOCOC <sub>6</sub> H <sub>5</sub>	m.p., 125°	—	—	26,00	2,98	6,14	28,02	—	72,5	5,12	—
				47,25	3,15	6,34	27,75	—	—	—	—
				47,08	5,26	12,33	—	—	—	—	—
				71,40	5,30	12,06	—	—	—	—	—
				71,72	—	—	—	—	—	—	—

Notes: <sup>1</sup>The i.r. spectrum had an intense absorption at 5.65  $\mu$  corresponding to C=N vibrations. <sup>2</sup>Mol. wt.: Found, 89.0; calculated, 83.0.<sup>3</sup>Mol. wt.: Found, 167.3; calculated, 166. <sup>4</sup>Obtained as an ether solution. Decomposed above -55°.

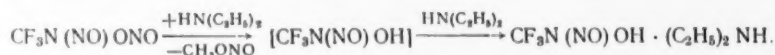
same crystalline anilide, N-phenyl-N'-tri(phenylamino) methylhydrazine, m.p. 134°. Perfluoroformimine monomer and dimer,  $\text{CF}_2 = \text{NF}$  and  $(\text{CF}_2\text{NF})_2$ , reacted with pyridine to form distillable complexes. The action of concentrated sulfuric acid on these complexes at 0° under vacuum gave the original monomer and dimer. The ability of these products to form complexes can be used for purification of the products from accompanying impurities. The preferential decomposition of the nitroso compound at the site of the C-N bond during pyrolysis is in agreement both with mass spectroscopy data (the formation by electron impact of an  $\text{NO}^+$   $M/e=30$  ion with a peak of maximum intensity at mass 30) and with the course of the decomposition of nitroso compounds under ultraviolet radiation. In the latter case, during photolysis of trifluoronitrosomethane, for example, both we and Haszeldine have demonstrated the formation of N,N-bistrifluoromethylhydroxylamine nitrite (b.p. +10°).



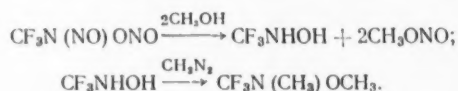
Since in these investigations the nitroso compound was in contact with nitric oxide formed during the reaction, it seemed of interest to study the behavior of polyfluorinated nitrosoalkanes toward nitric oxide. It was found that nitric oxide very readily reacts with the nitroso compounds at room temperature. When gaseous trifluoronitrosomethane and NO were mixed, the mixture immediately turned brown (formation of  $\text{N}_2\text{O}_4$ ), and a vacuum formed in the reaction vessel, although no appreciable decomposition of the nitro compound was noted during the first hours of the reaction. Thus, the nitroso compound catalyzes oxidation-reduction disproportionation of the nitric oxide. After several weeks, trifluoronitromethane and a certain amount of N,N-bistrifluoromethylhydroxylamine nitrite accumulated in the reaction system. The interaction of  $\text{CF}_3\text{NO}$  with NO can be represented as follows:



This scheme was confirmed by the reaction of  $\text{CF}_3\text{NO}$  and NO in solution (ether, petroleum ether, methanol) at low temperatures (-100°). One mole of  $\text{CF}_3\text{NO}$  combined with two moles of nitric oxide forming the bisnitroso derivative of trifluoromethylhydroxylamine, which decomposes rapidly at -50°. The action of a base on the bisnitroso derivative converted it to a comparatively stable salt of N-nitroso-N-trifluoromethylhydroxylamine:

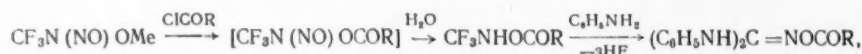


When it was heated to room temperature in the presence of an alcohol, a second nitroso group was split off, and N-trifluoromethylhydroxylamine was formed (isolated as the N,O-dimethyl derivative by reaction with diazomethane):



When the reaction of trifluoronitrosomethane with nitric oxide was carried out in alcohol in the presence of ferrous or cuprous salts, the reaction mixture being cooled with solid carbon dioxide, complex derivatives, for example,  $\text{CF}_3\text{N} \begin{smallmatrix} \text{NO} \\ \text{OHCuCl} \end{smallmatrix}$ , analogous to "cupferron" separated from solution.

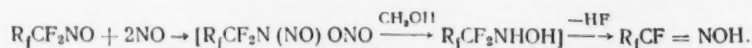
N-nitroso-N-trifluoromethylhydroxylamine salts are reactive. They are readily oxidized to trifluoronitromethane, and they react with acyl chlorides forming O-acyl-N-trifluoromethylhydroxylamine. A mixed ether,  $\text{CF}_3\text{OR}$ , is formed when the salts are boiled with methanol:



where  $\text{R} = \text{CH}_3$ ,  $\text{C}_6\text{H}_5$ ;  $\text{Me} = \text{Na}$ , etc.



Other polyfluorinated nitroso compounds, for example, 2-F-2-nitrosopropane, react with NO in a manner similar to trifluoronitrosomethane. In alcoholic medium, these reactions lead to fluorides of the corresponding polyfluoroalkylhydroxamic acids:



This study of the reactions of polyfluorinated nitrosoalkanes has shown that the nitroso group in these compounds is an active acceptor of free radicals, adding them at the site of the double bond; the nitroso derivative of hydroxylamine is readily formed with NO, i.e., nitrosoalkanes behave in this reaction in a manner analogous to the corresponding aromatic compounds [5-8].

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A STUDY OF THE STRUCTURE OF SOME COMPLEXES  
OF COPPER ACETATE AND CHLOROACETATES  
BY ELECTRON PARAMAGNETIC RESONANCE

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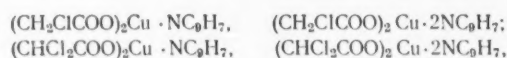
Original article submitted June 8, 1961

Amiel has found that paramagnetism of the  $\text{Cu}^{2+}$  ion in salts of fatty acids is approximately half its normal value [1]. Guha [2] found that the paramagnetic susceptibility of copper acetate monohydrate,  $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$  passes through a maximum at about room temperature and then rapidly decreases with a decrease in temperature, becoming zero at approximately 50°K. Lancaster and Gordi [3] measured the electron paramagnetic resonance (e.p.r.) of copper acetate powder in the millimeter region, and they observed only one line, with a g factor of approximately four. Bleaney and Bowers [4] studied the e.p.r. spectrum of a single crystal of this substance, and they proposed that the anomalous paramagnetism is due to the presence of isolated pairs in which the copper atoms are bonded by exchange forces. The interaction of the two spins leads, in this case, to the appearance of an upper triplet state with parallel spins ( $S=1$ ) and a lower singlet state with antiparallel spins ( $S=0$ ).

An x-ray investigation of copper acetate monohydrate crystals [5] showed that dimeric molecules actually do exist in the crystal lattice. The six nearest neighbors of the copper atom are four oxygen atoms belonging to the four acetate groups, a copper atom, and the oxygen of the water molecule. These six atoms are at the vertices of a distorted octahedron with the copper atom at its center. All interatomic distances between copper and oxygen of the carboxyl groups are approximately 1.97 Å. Each of the four acetate groups are separately planar. The distance between neighboring copper atoms is very small and is approximately equal to 2.64 Å, which is only a little greater than the distance in metallic copper (2.56 Å). The  $\text{Cu}-\text{H}_2\text{O}$  distance is 2.20 Å. Copper acetate monohydrate is a binuclear compound.

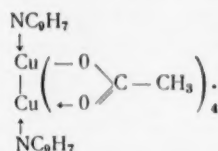
E.p.r. studies of single crystals of copper propionate monohydrate,  $(\text{CH}_3\text{CH}_2\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$  [6], copper *n*-butyrate monohydrate, and copper monochloroacetate monohydrate,  $(\text{CH}_2\text{ClCOO})_2\text{Cu} \cdot \text{H}_2\text{O}$  [7], have shown that the molecules are dimeric in these compounds also. There are no isolated copper ion pairs in the crystal lattice of copper trichloroacetate monohydrate  $(\text{CCl}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$  [7], and, therefore, the e.p.r. spectrum of this compound does not show a triplet state.

We have prepared copper monochloroacetate, which was obtained in the form of dark green prisms having the composition  $(\text{CH}_2\text{ClCOO})_2\text{Cu} \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , and have measured the e.p.r. spectrum of this salt. It proved to be due to transitions to the triplet state with an effective spin  $S=1$ . It appeared to be of interest to use e.p.r. to study the structure of complex compounds formed by the addition of nitrogen-containing ligands, such as ammonia, pyridine, and quinoline, to copper chloroacetate. Costăchescu and Ablov [8] showed that copper acetate and copper mono-, di-, and trichloroacetates all add quinoline. Copper acetate forms only one addition product, which contains one molecule of quinoline  $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{NC}_9\text{H}_7$ , while copper mono- and dichloroacetates yield the following additional products



and copper trichloroacetate forms only the addition product containing two molecules of quinoline. It should be added that all of the monoquinolinates were green, and the diquinolinates were violet.

A study of the e.p.r. spectra of certain of these products in the polycrystalline state at a frequency of 9330 Mcps (using a standard RE-type microwave spectrometer) showed that a triplet state, analogous to that of copper acetate monohydrate, was present in the case of the green copper acetate and monochloroacetate quinolinates. The Cu-Cu bond is retained in these compounds, and the green products are actually dimeric molecules having the composition



An experiment showed that a decrease in temperature from room temperature to 77°K leads to a decrease in the integral intensity of the paramagnetic resonance absorption. This confirms that the paramagnetism of these salts is due to an excited triplet state.

It is interesting to note that copper acetate monopyridinate  $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{NC}_5\text{H}_5$ , which is also green, also shows a triplet state with an effective spin  $S=1$ .

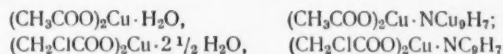
It is known [4] that in copper acetate monohydrate, the electric crystal field has almost axial symmetry and splits the triplet state into a singlet and doublet, which are separated by about  $0.34 \text{ cm}^{-1}$ . Therefore, two e.p.r. lines are observed in the 3-cm region, one of which is located in the very weak magnetic field, and the other of which is located at about 5000 oe. In polycrystalline samples, each of these lines is the result of averaging of anisotropic D parameters and g values.

TABLE 1. Positions of e.p.r. Lines and Values of the Fine Splitting Parameter, D

Substance	1st line (H, oe)	2nd line (H, oe)	D, $\text{cm}^{-1}$
$(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$	150	4460	0,34
$(\text{CH}_2\text{ClCOO})_2\text{Cu} \cdot 2\frac{1}{2}\text{H}_2\text{O}$	390	4580	0,36
$(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{NC}_5\text{H}_5$	360	4530	0,35
$(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{NC}_9\text{H}_7$	340	4560	0,35
$(\text{CH}_2\text{ClCOO})_2\text{Cu} \cdot \text{NC}_9\text{H}_7$	680	4630	0,40

If it is assumed that for the compounds investigated, it is possible to characterize the fine splitting by a single D parameter, then its average value is easily evaluated by comparing the e.p.r. spectra of these substances with the spectrum of copper acetate monohydrate. Table 1 shows that both lines of  $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{NC}_9\text{H}_7$ ,  $(\text{CH}_2\text{ClCOO})_2\text{Cu} \cdot \text{NC}_9\text{H}_7$ , and  $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{NC}_5\text{H}_5$  are shifted in the direction of a stronger field, which indicates an increase in the D parameter of these substances. The values of D presented in Table 1 were determined from the relative distances of the strong-field lines from the e.p.r. signal of  $\alpha, \alpha$ -diphenyl- $\beta$ -picrylhydrazyl.

It should be noted that the e.p.r. spectra of copper acetate monoquinolate and monopyridinate differed very little from each other, both with respect to position and width of the lines and with respect to D value. Upon comparing the e.p.r. spectra of the compounds

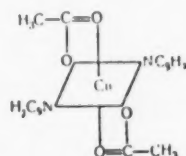


it is apparent that replacement of a hydrogen in the methyl group by a chlorine leads to an increase in fine splitting and the increase is greater in the case of the quinolinates than in the case of the hydrates.

TABLE 2. g-Factors and e.p.r. Line Widths in  $\Delta H$ , Measured between Points of Maximum Slope

Substance	g	$\Delta H$ , oe
$(\text{CH}_2\text{ClCOO})_2\text{Cu} \cdot 2\text{NC}_9\text{H}_7$	2.06	28
$(\text{CCl}_3\text{COO})_2\text{Cu} \cdot 2\text{NC}_9\text{H}_7$	2.08	170

The e.p.r. spectra of the violet copper monochloro- and trichloroacetate diquinolinates show that we have here a singlet state with a spin  $S=\frac{1}{2}$ . This serves as an indication that there are no Cu-Cu bonds in these products. These compounds most probably have the following structure:



The possibility cannot be excluded that four of the vertices of the distorted octahedron (square bipyramid) are occupied by oxygens of four, not two, acetate groups. Values of the effective g factor and line widths measured between points of maximum slope are given in Table 2.

The e.p.r. spectrum of copper acetate diammoniate,  $(\text{CH}_3\text{COO})_2\text{Cu} \cdot 2\text{NH}_3$ , which is also violet colored, also displayed only a singlet state. The e.p.r. signal was a very asymmetric line, the form of which was retained even after careful powdering of the crystals. This is due to the high anisotropy of the g factor and the line widths. An x-ray investigation and a study of the e.p.r. spectrum of single crystals of this compound are presently in progress in our laboratories.

The authors consider it their agreeable duty to express their appreciation to Prof. B. M. Kozyrev for his interest in this work and for very valuable discussions of the results.

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# THE FREE ENERGY OF FORMATION OF MANGANESE

## CARBIDE $Mn_{23}C_6$

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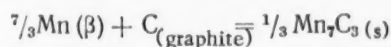
Original article submitted June 7, 1961

Manganese enters into almost all construction steels, and, in addition, it is used as an alloying element. The effect of manganese on the properties of steel depends to a significant extent on its interaction with carbon [1]. However, data on the thermodynamic properties of manganese carbides are presently insufficient. According to reference [2], five carbides exist in the system Mn-C:  $Mn_{23}C_6$  (stable up to 1025°C),  $Mn_7C_3$  (stable between 850-1000°),  $Mn_3C$  (stable between 950 and 1050°),  $Mn_5C_2$  (stable up to 1050°), and  $Mn_7C_3$  (stable up to 1100°). Not all of these carbides were observed in earlier work, and the existence of only the carbide  $Mn_3C$  was assumed.

In view of the existing uncertainty regarding data on the composition and nature of manganese carbides, there is also uncertainty in the results obtained during studies of their thermodynamic properties. Thus, for example, Ulich and Siemonsen [3] determined the heat of combustion of  $Mn_3C$ , and thereby obtained a value of -3.6 kcal ( $\pm 1.0$  kcal) for the heat of formation ( $\Delta H$ ). However, this value is -17.0 kcal according to the measurements of Roth [4]. It can be assumed that such contradiction is due to uncertainty regarding the phase composition of the samples examined by these authors.

We may remark that the heats of formation ( $\Delta H$ ) of the carbides of the two elements neighboring manganese—chromium and iron ( $Cr_{23}C_6$  and  $Fe_3C$ )—are, respectively, -13.6 kcal and +5.4 kcal per g-atom of carbon. Hence, it appears that the result of Ulich and Siemonsen is closer to the actual value than the result of Roth.

A recently published article [5] presented data on the free energy of formation of the manganese carbide  $Mn_7C_3$ . Measurements of the vapor pressure of manganese over a mixture of this carbide and pure graphite in combination with data for the vapor pressure of pure manganese [5] gave for the reaction



the following expression for the free energy

$$\Delta G^0_{1075-1235^\circ K} = 5130 - 11,64T.$$

Thus, up to the present time, only two ( $Mn_3C$  and  $Mn_7C_3$ ) of the existing five manganese carbides have been subjects of thermodynamic investigations.

The present communication reports the results of a determination of the free energy of formation of the manganese carbide having the lowest carbon content  $Mn_{23}C_6$ . Equilibrium in the system  $Mn_{23}C_6-H_2-Mn-CH_4$  was investigated using the previously described circulation method [6]. The carbide was prepared by sintering a mixture of powdered metallic manganese (99.77% Mn, 0.08% C, and 0.103% S) and carbon black at a temperature of 1050°C for a day in an atmosphere of argon.

Figure 1 shows an x-ray photograph of the sample used in carrying out the experiments (the photograph was taken with unfiltered chromium radiation). Interference lines 1,3,8,9,10,11,12,15,17,18, and 20 relate to the carbide  $Mn_{23}C_6$ ; the remaining lines (2,5,6,7,13,14,16,19,21, and 22) relate to metallic manganese. Some of the interference lines on the pattern (for example, lines 1,3, and 6) can be equally assigned both to the carbide phase and to metallic manganese. The lines appearing on the pattern shown in Fig. 1 were identified by means of the tables given

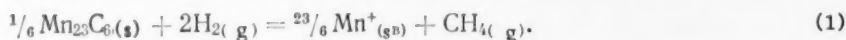


in reference [7] (for the carbide  $\text{Mn}_{23}\text{C}_6$ ). Interplanar distances for metallic manganese were first calculated from an x-ray pattern for electrolytic Mn.



Fig. 1. X-ray photograph of a sample consisting of two phases—the carbide  $\text{Mn}_{23}\text{C}_6$  and metallic manganese. Lines 1,3,8,9,10,11,12,15,17,18, and 20 relate to the carbide phase; the remaining lines relate to metallic manganese (taken with unfiltered chromium radiation).

An x-ray phase investigation of the sample after the experiments showed that two phases, namely  $\text{Mn}_{23}\text{C}_6$  and Mn, were still present in the sample. Therefore, it may be presumed that the equilibrium constant  $K_p = P_{\text{CH}_4} / P_{\text{H}_2}^2$  for the reaction:



was determined in these experiments. The value of  $K_p$  was determined over the temperature interval from 650 to 900°C. The experimental results are shown in Fig. 2, where  $\log K_p$  is plotted as a function of  $1/T$ . Difficulties were encountered in the study of equilibrium (1) owing to considerable distillation of the metallic manganese and condensation on the cold parts of the apparatus. This could have led to some change in the composition of the gas phase as a consequence of adsorption of methane and hydrogen by the condensed manganese. Moreover, the high volatility of manganese prevented degassing of the sample at the required temperature. The scatter in the experimental results apparently resulted from these causes.

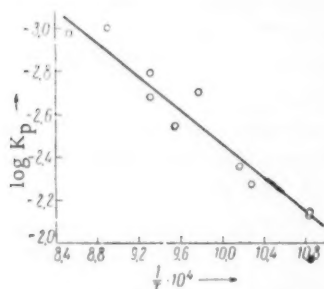


Fig. 2. Dependence of  $\log K_p$  on  $1/T$  for the reaction  $\frac{1}{6} \text{Mn}_{23}\text{C}_6(\text{s}) + 2\text{H}_2(\text{g}) = \frac{23}{6} \text{Mn}(\text{s}) + \text{CH}_4(\text{g})$ .

A least squares treatment of the data shown in Fig. 2 leads to the equation

$$\log K_{p923-1173^\circ\text{K}} = \frac{4000 (\pm 380)}{T} - 6.45 (\mp 0.45); \quad (2)$$

$$\Delta G_{923-1173^\circ\text{K}}^\circ = -18300 (\pm 1700) + 29,51 (\mp 2,0) T. \quad (3)$$

Combination of Eq. (3) with the equation for the free energy of formation of methane [8] gives

$$\frac{23}{6} \text{Mn}(\text{s}) + \text{C}_{(\text{graphite})} = \frac{1}{6} \text{Mn}_{23}\text{C}_6(\text{s}) \quad (4)$$

$$\Delta G_{973-1173^\circ\text{K}}^\circ = -3300 (\pm 1700) - 3,35 (\mp 2,0) T. \quad (5)$$

Hence, it follows that the heat of formation of  $\text{Mn}_{23}\text{C}_6$  (-3300 cal) is very close to the value found by Ulich and Siemonson for a carbide which these authors considered to correspond to the formula  $\text{Mn}_3\text{C}$ . Since x-ray structural analysis was not used in the work reported in reference [3], it may be assumed that the results of that work relate to the same carbide investigated in the present investigation. In this case, it may be considered that agreement between the values for the heat of formation of  $\text{Mn}_{23}\text{C}_6$  found by Ulich and Siemonson and by us is satisfactory.

It is interesting to compare our thermodynamic data, which relate to  $\text{Mn}_{23}\text{C}_6$ , with the corresponding data for  $\text{Mn}_7\text{C}_3$  [5]. While the carbide  $\text{Mn}_{23}\text{C}_6$  is formed with an evolution of heat, the carbide with the greater carbon content,  $\text{Mn}_7\text{C}_3$ , is an endothermic compound. This fact can be interpreted on the basis of the following considerations. According to existing concepts appearing in the literature, during the formation of carbides of transition metals of the fourth period there is partial filling of the  $d$  orbital of the metal atoms by valence electrons of the carbon atoms. Since the electrons experience a mutual repulsion, as the vacancies in this orbital are filled the energy of the added

electrons increases. Therefore, the heat of formation of carbides decreases with an increase in the degree of filling of the  $d$  orbital by electrons. This increase in the degree of filling takes place both with an increase in the atomic number of the metal in the series  $Ti \rightarrow Ni$  and with an increase in the ratio of the number of carbon atoms to the number of metal atoms in the carbides. The known fact that there is a decrease in the affinity of metals for carbon in the series  $Ti \rightarrow Ni$  supports the first of these considerations.

The second consideration is in agreement with the result, cited above, of the comparison of the heats of formation of the two manganese carbides  $Mn_{23}C_6$  and  $Mn_7C_3$ .

We note that chromium is an exception with respect to affinity for carbon in the series  $Ti \rightarrow Ni$ . Thus, the heat of formation of the chromium carbide  $Cr_{23}C_6$ , -13600 cal per g-atom of carbon [9], exceeds the heat of formation of vanadium carbides (for example, the heat of formation of  $V_2C$  is -11500 cal [6]). The existence of such an anomaly permits an assumption as to the relative roles of  $s$  and  $d$  electrons of transition metal atoms during carbide formation. The electronic structure of the free chromium atom differs from that of the atoms of its neighbors in the periodic system (manganese and vanadium) in that it contains only one  $4s$  electron instead of the two in Mn and V. In addition, the  $d$  orbital of the chromium atom contains just as many electrons as the  $d$  electrons as the  $d$  orbital in the manganese atom and, correspondingly, two more electrons than the  $d$  orbital of the vanadium atom. Hence, it is possible to assume that in the formation of chromium carbides, a covalent bond can be formed by pairing of one of the valence electrons of the carbon with the  $4s$  electron of the chromium. It is apparently for this reason that the heat of formation of  $Cr_{23}C_6$  both exceeds the heats of formation of the vanadium carbides and considerably exceeds the heat of formation of the manganese carbide  $Mn_{23}C_6$ , which is isomorphic with  $Cr_{23}C_6$ .

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# ON THE INTERACTION OF IMIDO ESTERS WITH ALKYL HALIDES

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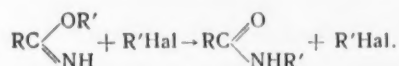
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In 1899; Wheeler and Johnson showed that the interaction of imido esters with alkyl halides at temperatures of 100-150° converts the imido ester to an N-substituted amide of the carboxylic acid [1].

The rearrangement can be expressed in general form by



If the alkyl halide and the ester group have identical radicals, the resulting amide is an isomer of the original imido ester. If these radicals are different, the radical attached to the nitrogen of the resulting amide may be either that of the ester group or the radical originally belonging to the alkyl halide. Alkyl esters of aliphatic and aromatic imidic acids, with or without a substituent at the nitrogen, can enter into the arrangement [1-3].

The present work constitutes the first part of an investigation in the field of imido esters, which we undertook with the aim of further studying the interaction of imido esters with alkyl halides. The reaction of a series of imido esters with the ethyl iodide, benzyl iodide, benzyl bromide, and triphenylmethyl bromide was studied.

TABLE 1. Imido Esters of the Composition  $\text{C}_6\text{H}_5\text{C} \begin{array}{c} \text{OR} \\ \diagup \\ \text{NC}_6\text{H}_5 \end{array}$

R	M.p., °C	B.p., °C/mm	$d_4^{20}$	$n_D^{20}$	Empirical formula	MRD		N %		Yield, %
						found	calc.	found	calc.	
iso-C <sub>3</sub> H <sub>7</sub>	43-44	162-163°/10	—	—	C <sub>16</sub> H <sub>17</sub> NO	—	—	6,07 6,19	5,85	72
n-C <sub>4</sub> H <sub>9</sub>	—	179-181°/10	1,0289	1,5468	C <sub>17</sub> H <sub>19</sub> NO	78,06	77,82	5,68 5,75	5,52	43
iso-C <sub>4</sub> H <sub>9</sub>	—	174,5- 175°/10	1,0278	1,5450	C <sub>17</sub> H <sub>19</sub> NO	77,92	77,82	5,59 5,78	5,52	37
iso-C <sub>5</sub> H <sub>11</sub>	—	149- 150°/0,6	1,0134	1,5395	C <sub>18</sub> H <sub>21</sub> NO	82,71	82,44	5,67 5,72	5,23	45

Four previously undescribed higher alkyl esters of N-phenylbenzimidic acid were synthesized, and their behavior with respect to alkyl halides was investigated. Table 1 contains some properties of the newly synthesized imido esters. Constants of previously described imido esters are not given. All imido esters used in this work were synthesized by a well-known method [4]: by the reaction between N-phenylbenzimidoyl chloride, prepared by the method of reference [5], and the appropriate sodium alcoholate in an alcohol-ether medium.

The reaction of the imido ester with the alkyl halide was carried out in a sealed glass tube. The conditions for all of the reactions and the yields of the major products are shown in Table 2. The percentage yield of the major product is simultaneously the percentage conversion of the imido ester; in each case, the corresponding amount of unreacted imido ester was recovered from the reaction mixture. Separation of the amides and imido esters was carried out by vacuum distillation, or it was based on their difference in solubility.

N-Phenylbenzimidic acid ethyl ester was quantitatively isomerized to N-ethylbenzanilide by heating it with

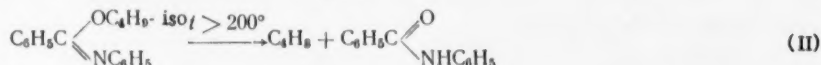
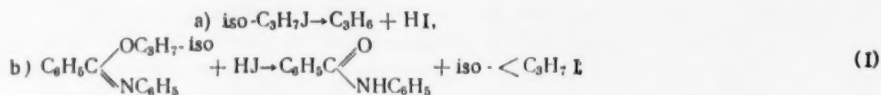
ethyl iodide at 155° for 10 hours. This result is in good agreement with the data of Lander [3], who almost completely isomerized this imido ester with ethyl iodide in 13 hours at 150-160° with a reagent ratio (molar) of 1:0.5. The reaction with benzyl bromide led to rearrangement with the formation of N-benzylbenzanilide. The absence of N-ethylbenzanilide among the reaction products allowed us to conclude that the benzyl radical is considerably more active than ethyl in the reaction with imido esters under the same conditions. The imido ester did not undergo rearrangement in the presence of triphenylmethyl bromide. The reagents underwent no change at temperatures up to 140°, and above this temperature, the reaction product was a water- and alcohol-insoluble tar from which individual compounds could not be separated.

TABLE 2

Imido ester	Alkyl halide	Ratio of reagents, molar	Reaction temp., °C	Reaction time, hours	Major reaction product	
					Compound	Yield
$\text{C}_6\text{H}_5\text{C}(\text{OC}_2\text{H}_5)=\text{NC}_6\text{H}_5$	$\text{C}_2\text{H}_5\text{I}$	1:1	155	10	$\text{C}_6\text{H}_5\text{C}(\text{O})=\text{N}(\text{C}_6\text{H}_5)_2$	98
$\text{C}_6\text{H}_5\text{C}(\text{OC}_2\text{H}_5)=\text{NC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{CH}_2\text{I}$	1:1	100 155	3 7	$\text{C}_6\text{H}_5\text{C}(\text{O})=\text{N}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	90
$\text{C}_6\text{H}_5\text{C}(\text{OC}_2\text{H}_5)=\text{NC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	1:1	155 210	8 1.5	$\text{C}_6\text{H}_5\text{C}(\text{O})=\text{N}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	98
$\text{C}_6\text{H}_5\text{C}(\text{OC}_2\text{H}_5)=\text{NC}_6\text{H}_5$	$(\text{C}_6\text{H}_5)_3\text{CBr}$	1:1	140-180	—	Tar	
$\text{C}_6\text{H}_5\text{C}(\text{OCH}_2\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{CH}_2\text{I}$	1:1	155	8	$\text{C}_6\text{H}_5\text{C}(\text{O})=\text{N}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	96
$\text{C}_6\text{H}_5\text{C}(\text{OCH}_3)=\text{NC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{CH}_2\text{I}$	1:1	155	8	1) $\text{C}_6\text{H}_5\text{C}(\text{O})=\text{N}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$ 2) $\text{C}_6\text{H}_5\text{C}(\text{O})=\text{N}(\text{C}_6\text{H}_5)\text{CH}_3$	46 35
$\text{C}_6\text{H}_5\text{C}(\text{OC}_3\text{H}_7)=\text{NC}_6\text{H}_5$ iso	iso- $\text{C}_4\text{H}_9\text{I}$	1:1	155	17	$\text{C}_6\text{H}_5\text{C}(\text{O})=\text{NHC}_4\text{H}_9$	40
$\text{C}_6\text{H}_5\text{C}(\text{OC}_3\text{H}_7)=\text{NC}_6\text{H}_5$ iso	$\text{CH}_3\text{I}$	1:1.2	100-155	14	$\text{C}_6\text{H}_5\text{C}(\text{O})=\text{N}(\text{C}_6\text{H}_5)\text{CH}_3$	61
$\text{C}_6\text{H}_5\text{C}(\text{OC}_6\text{H}_5)=\text{H}$	$\text{C}_6\text{H}_5\text{I}$	1:2	155-212	17.5	$\text{C}_6\text{H}_5\text{C}(\text{O})=\text{NHC}_6\text{H}_5$	35
$\text{C}_6\text{H}_5\text{C}(\text{OC}_6\text{H}_5)=\text{H}$	$\text{CH}_3\text{I}$	1:1.3	100-155	16	$\text{C}_6\text{H}_5\text{C}(\text{O})=\text{N}(\text{C}_6\text{H}_5)\text{CH}_3$	37
$\text{C}_6\text{H}_5\text{C}(\text{OC}_4\text{H}_9)=\text{iso}$	iso- $\text{C}_4\text{H}_9\text{I}$	1:1	155-210	19.5	$\text{C}_6\text{H}_5\text{C}(\text{O})=\text{NHC}_4\text{H}_9$	23
$\text{C}_6\text{H}_5\text{C}(\text{OC}_4\text{H}_9)=\text{iso}$	$\text{CH}_3\text{I}$	1:1	100-155	19	$\text{C}_6\text{H}_5\text{C}(\text{O})=\text{N}(\text{C}_6\text{H}_5)\text{CH}_3$	46
$\text{C}_6\text{H}_5\text{C}(\text{OC}_5\text{H}_{11})=\text{iso}$	$\text{CH}_3\text{I}$	1:1	155	10	$\text{C}_6\text{H}_5\text{C}(\text{O})=\text{N}(\text{C}_6\text{H}_5)\text{CH}_3$	31

N-Phenylbenzimidic acid benzyl ester was quantitatively isomerized by benzyl iodide. Two amides, N-benzylbenzanilide and N-methylbenzanilide, were formed during the interaction of N-phenylbenzimidic acid methyl ester with benzyl iodide; the first of these was formed in the greater amount. Benzyl iodide is apparently a more active reagent in this reaction than methyl iodide.

Higher (beginning with isopropyl) esters of N-phenylbenzimidic acid were not isomerized by the corresponding alkyl iodides; benzanilide and the corresponding olefin were formed. The reaction evidently proceeds by one of the schemes:



The decomposition of N-phenylbenzimidic acid sec-butyl ester in accordance with scheme (II) has been demonstrated during an attempt to isomerize it thermally [6]. The reaction with methyl iodide proceeds with the formation of N-methylbenzanilide; i.e., rearrangement takes place.

On this basis of our experiments and the literature data [1-3], the above halides can be arranged in the following series of decreasing activity in rearrangement reactions of imido esters:  $\text{C}_6\text{H}_5\text{CH}_2\text{I} > \text{CH}_3\text{I} > \text{C}_6\text{H}_5\text{CH}_2\text{Br} > \text{C}_2\text{H}_5\text{I} > \text{C}_3\text{H}_7\text{I} > \text{C}_2\text{H}_5\text{Br}$ .

Higher alkyl iodides apparently do not enter into the rearrangement reaction.

#### EXPERIMENTAL

1. N-Phenylbenzimidoyl chloride. A mixture of 50 g of benzanilide and 52 g of phosphorus pentachloride were placed in a distillation flask fitted with an outlet tube protected from atmospheric moisture, and stirring was commenced. The flask was heated on a water bath, and a vigorous reaction began; hydrogen chloride was evolved, and the reaction mixture liquified. At the conclusion of the reaction, the phosphoryl chloride was distilled under vacuum. The residue was dissolved in 100 ml of dry ether, and, after filtration, the solution was used for the synthesis of the imido ester.

2. N-Phenylbenzimidic acid isopropyl ester. a) The reaction vessel consisted of a 500-ml round-bottom, three-neck flask fitted with a stirrer, a tube for the introduction of hydrogen into the mixture, and a reflux condenser protected from atmospheric moisture. To the flask were charged 200 ml of absolute isopropyl alcohol and 6 g of sodium. To the cooled crystalline sodium isopropylate was added dropwise an ether solution of the imido chloride, prepared from 50 g of benzanilide. A white turbidity, caused by the formation of sodium chloride, formed immediately. Upon completion of the reaction, the yellowish orange solution was separated from the sodium chloride and distilled. Two distillations yielded 43.6 g of the imido ester with a b.p. of 162-163° at 10 mm; the yield was 72% based on the benzanilide. The product completely crystallized after the distillation; m.p. 43-44°. Found %: C 80.49; 80.27; H 7.17; 7.43; N 6.07; 6.19.  $\text{C}_{16}\text{H}_{17}\text{ON}$ . Calculated %: C 80.30; H 7.16; N 5.85.

b) The reaction was carried out under the conditions of the preceding experiment, but the reaction mixture was treated with cold water, part of the ether was distilled, and the residue was decanted into cold water. The resulting oil rapidly crystallized. The product was recrystallized three times from dilute alcohol. The yield was 53%. M.p., 43-44°. The crystals were yellowish needles, and had a slight odor.

The following esters of N-phenylbenzimidic acid were synthesized in experiments similar to a): methyl, ethyl, benzyl, n-butyl, isobutyl, and isoamyl. All of these esters are syrupy liquids with a greenish yellow color and a slight odor. They are soluble in alcohol, ether, ethyl acetate, aliphatic, and aromatic hydrocarbons, and alkyl halides. They are insoluble in water. They are hydrolyzed by dilute mineral acids; rupture occurs at the C=N bond, and alkyl benzoates and aniline are formed.

3. Reaction of N-phenylbenzimidic acid ethyl ester with benzyl iodide. A mixture of 8 g of the imido ester and 7.8 g of benzyl iodide (molar ratio of 1:1) was sealed in a glass tube. The tube was heated for 3 hours at 100° and for 7 hours at 155°. The reaction mixture was poured into a distillation flask, and the ethyl iodide was distilled at atmospheric pressure. Nothing distilled from the residue at a pressure of 10 mm and a bath temperature up to 180-200°. The mass crystallized when poured into a casserole and triturated with ether. Two recrystallizations from alcohol produced small white prisms of N-benzylbenzanilide. The amount was 9.0 g (90%). M.p., 105-106°. Found %: N 4.97; 5.09.  $\text{C}_{20}\text{H}_{17}\text{NO}$ . Calculated %: N 4.88.

The literature [7] reports an m.p. of 105°.



In the manner previously described, seven alkyl esters of N-phenylbenzimidic acid were synthesized, and their reactions with alkyl halides were studied. It was shown that higher alkyl imido esters are not isomerized by the corresponding alkyl halides, but they do enter into a rearrangement with methyl iodide.

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# METHODS FOR STUDYING THE STABILITY OF PHTHALOCYANINE COMPLEX COMPOUNDS

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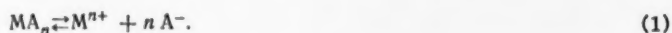
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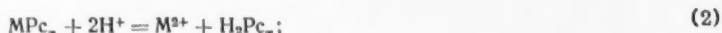
Original article submitted June 22, 1961

Presently known methods for investigating complex compounds [1] have been successfully applied only to the study of comparatively unstable complexes, i.e., complexes which clearly dissociate in solution into the component ions:



With an increase in the degree of covalency of the M-A bonds, the ions forming the complex more closely approach the state of neutral atoms [2]; the bond loses its ionic character and thereby its ability to break with the formation of ions, and the compound acquires the ability to dissociate into electrically neutral particles. It is for this reason that, in the case of solutions of particularly stable complex compounds, for example, complexes formed by ions of the typical complex formers  $Co^{3+}$ , Pt, and Pd with a large number of ligands and also by numerous cations with such important ligands as porphyrin, pentadienyl, carbonyl, and phthalocyanine, the stability becomes impossible to characterize by a stability constant. In addition to the insignificant dissociation into ions, there is an additional reason which forbids the use of stability constants in connection with a number of complex compounds. There has been some mention of complexes with unstable dissociation products, for which an apparent irreversibility of the dissociation process is intrinsic.

The metal phthalocyanines, which are the subject of the present paper, appreciably dissociate only in media of protonic acids.\*



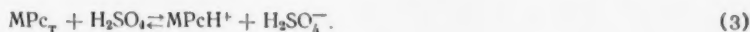
Process (2) takes place in the solid phase, and process (2a) proceeds in  $H_2SO_4$  with a concentration of above 8 m/liter. Our investigations showed that processes (2) and (2a) take place rapidly and irreversibly for labile phthalocyanines formed by alkali and alkaline earth metal cations and also by  $Hg^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Mg^{2+}$ ,  $Be^{2+}$ ,  $Ag^+$ ,  $Fe^{2+}$ . We should also add to this list  $Sb^{3+}$ ,  $Mn^{2+}$ ,  $Sn^{2+}$ , and phthalocyanines.

Stable phthalocyanines formed by  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Pt^{2+}$ ,  $Pd^{2+}$ ,  $V^{4+}$ ,  $AlCl_2^{2+}$  and, particularly,  $SnCl_2^{2+}$  do not react in accordance with schemes (2) and (2a) to any appreciable extent [3]. The lack of isotope exchange between  $MPcH^+$  and  $Co^{2+}$ -60 in  $H_2SO_4$  solution, which should take place in reactions following scheme (2a), and a study of reaction (2) with radioactive  $CoPc$  and  $ZnPc$  showed that the stable phthalocyanines dissociate irreversibly by schemes (2) and (2a) in aqueous acid media. Thus, in spite of appreciable ionic dissociation in an acid medium, the phthalocyanines cannot be characterized by means of the equilibrium constant of (2) or (2a), since the dissociation process is irreversible in aqueous acid media. However, the question of the order of stability of extremely stable complex compounds is of extreme significance to the chemistry of complexes [2]. It is of interest in connection with the metal phthalocyanines, since, in the first place, phthalocyanine is an extremely specific ligand, and, in the second place, the phthalocyanines are related to a group of important physiologically active porphyrin derivatives [4,5].

\*Pc is an arbitrary symbol for the doubly charged tetrabenzotetrazaporphine (phthalocyanine) anion.  $M^{2+}$  is a metal ion.

In those cases where it is impossible or difficult to determine the instability constant or to carry out thermodynamic measurements of the metal-to-ligand bond energy, the following methods are used to characterize the stability of the complex: 1) isotope exchange [6], 2) measurement of the shift in the long-wave bands corresponding to an electronic transition in the ligand [7], 3) measurement of the shift in the bands of the i.r. spectrum [8], 4) proton magnetic resonance [9], and 5) measurement of the rate of cleavage of the metal by the action of acids [10]. The two latter methods are the least known.

Using phthalocyanine complexes, we investigated the possibility of using method (5), first studying the form in which the phthalocyanines exist in  $H_2SO_4$  at different temperatures and certain properties of sulfuric acid as a solvent. It has previously been shown [11-13] that phthalocyanines behave as monacidic bases in strong  $H_2SO_4$  at ordinary temperature:



Equilibrium constants for reaction (3) at 25°, calculated by the method of reference [11], are shown in Table 1. The constants for industrially important phthalocyanines were measured at different temperatures (Table 2). Two important conclusions follow from a review of the constants. The constants remain constant at all temperatures. This

TABLE 1. Equilibrium Constant Exponent, pK, for the Solution of Stable Phthalocyanines in  $H_2SO_4$  at 25°

Phthalocyanine	pK = -log	Phthalocyanine	pK = -log
H <sub>2</sub> Pc	1,65 ± 0,02	CuPc	1,64 ± 0,03
NiPcCl	1,46 ± 0,03	CuPcCl <sub>15</sub>	2,82 ± 0,04
PdPcCl	1,52 ± 0,05	ZnPc	2,31 ± 0,04
PtPcCl	1,50 ± 0,06	(SO <sub>4</sub> ) VPc	1,92
CoPcCl	2,06 ± 0,04	(HSO <sub>4</sub> ) AlPc	2,60
		(HSO <sub>4</sub> ) <sub>2</sub> SnPc	3,52

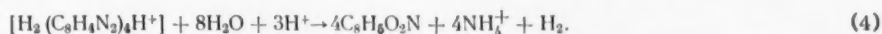
is additional confirmation that strong  $H_2SO_4$  displays the properties of an ideal solvent [14-16], owing to which the ratio of the activity coefficients of the participants in reaction (3) remains constant, and complete dissociation of the reaction product,  $(MPcH)H_2SO_4$ , is attained. That the constants are constant proves the correctness of scheme (3) and, together with spectroscopic data [12], confirms the prevalence of  $MPcH^+$  ions in  $H_2SO_4$  solutions. The dependence of the equilibrium constant exponent (pK) of reaction (3) on the nature of the metal is due, in our opinion [11], mainly to the nature of the chemical bonds of the metals with the ligand and to their stability. The pK values make it possible to form an opinion as to the formation and strength of the  $\sigma$ - and  $\pi$ - bonds and, consequently, as to the

stability of the MPc, the presence of an excess charge on the central ion, and the inductive effect of substituents on the benzene ring [13]. Calculation of the change in the thermodynamic functions (Table 3) of reaction (3) revealed the presence of an endothermic effect which decreased with an increase in the solvability of the phthalocyanine owing to the ability of the central ion to undergo additional coordination (ZnPc, ZnPcCl) [17], the presence of a charge on the central ion ( $^+AlPcCl$ ), or polarization of the bonds [13] during chlorination of the benzene rings (CuPcCl<sub>15</sub>). These proposals are also confirmed by the magnitudes of the entropy changes in reaction (3).

TABLE 2. Temperature Dependence of the pK of Phthalocyanines in  $H_2SO_4$

Temp., °C	pK of metal phthalocyanines				
	CuPc	CuPcCl <sub>15</sub>	ZnPcCl	ZnPc	CoPcCl
20	1,75 ± 0,04	—	—	2,31 ± 0,01	—
25	1,64 ± 0,03	—	—	—	2,07 ± 0,01
30	1,52 ± 0,02	2,81 ± 0,04	1,52 ± 0,05	—	—
40	1,43 ± 0,04	2,70 ± 0,03	1,45 ± 0,04	—	1,78 ± 0,01
50	1,29 ± 0,06	2,65 ± 0,03	1,40 ± 0,02	1,95 ± 0,03	1,66 ± 0,06
70	1,54 ± 0,02	2,70 ± 0,01	1,60 ± 0,03	—	1,72 ± 0,01

As noted in the literature [5], phthalocyanines decompose in  $H_2SO_4$  solutions. The process is accompanied by complete hydrolysis at the macro ring:



The color of the  $MPcH^+$  and  $H_2PcH^+$  disappears during this reaction. We carried out a detailed study of the hydrolysis of the macro ring of a free phthalocyanine ( $H_2PcH^+$ ) and studied the effect of the nature of the central ion on hy-

hydrolysis. It was found that all labile phthalocyanines hydrolyze by the same process as the hydrolysis of a free phthalocyanine. Reaction (2a) takes place rapidly; the limiting step is hydrolysis of the macro ring of the  $H_2PcH^+$  by reaction (4), which is described by a first order kinetic equation:

$$-\frac{dC_{MPc}}{dt} = k_{exp} C_{MPc}$$

$k_{exp}$  depends on the concentration  $[H_3O^+]$ , and it is connected with  $[H_3O^+]$  by the equation  $k_{exp} = k_t \cdot [H_3O^+]^4$ .

TABLE 3. Change in Thermodynamic Properties During Solution of Phthalocyanines in Sulfuric Acid

Phthalocyanine	$\Delta H^\circ_{298}$ , cal/mole	$\Delta F^\circ_{298}$ , cal/mole	$\Delta S^\circ_{298}$ , e.u.
CuPc	$5700 \pm 600$	$2235 \pm 40$	$11,6 \pm 2,1$
CoPcCl	6810	2820	13,4
ZnPcCl	2930	2110	2,76
ZnPc	5230	3060	7,28
+AlPcCl	4220	3542	2,26
CuPcCl <sub>15</sub>	3660	3790	-0,44

TABLE 4. Rate Constants,  $k_{exp}$ , for Hydrolysis of Labile Phthalocyanines at 25°

Phthalocyanine	H <sub>2</sub> SO <sub>4</sub> , conc., m/liter	$k_{exp}$ , hours <sup>-1</sup>	Phthalocyanine	H <sub>2</sub> SO <sub>4</sub> , conc., m/liter	$k_{exp}$ , hours <sup>-1</sup>
H <sub>2</sub> Pc	17,65	$0,137 \pm 0,008$	PbPc	17,65	$0,109 \pm 0,008$
	15,40	$5,30 \pm 0,14$		15,40	$5,08 \pm 0,23$
MgPc	17,65	$0,113 \pm 0,011$	SnPc	17,65	$0,145 \pm 0,024$
	15,40	$3,40 \pm 0,26$		15,40	$2,26 \pm 0,42$
CdPc	17,65	$0,103 \pm 0,007$	ClFePc	17,65	$0,198 \pm 0,014$
	15,40	$4,60 \pm 0,13$		15,40	$0,566 \pm 0,018$
					(light)
AgPc	17,65	$0,170 \pm 0,010$		15,40	$0,550 \pm 0,025$
	15,40	$0,78 \pm 0,20$			(dark)
			Cl <sub>2</sub> SnPc	17,65	$0,0155 \pm 0,0014$
				15,40	$0,160 \pm 0,018$

TABLE 5. Hydrolysis Rate Constants ( $k_{exp}$  hours<sup>-1</sup> · 1000) of Stable Pythalo-cyanines

Phthalocyanine	18,2 M H <sub>2</sub> SO <sub>4</sub>		16,20 M H <sub>2</sub> SO <sub>4</sub>	
	100 °	120 °	100 °	120 °
CuPc	$10,4 \pm 0,4$	$185 \pm 12$	—	$815 \pm 57$
ZnPc	$280 \pm 20$	$3930 \pm 130$	—	—
(SO <sub>4</sub> ) VPc	—	—	$2200 \pm 60$	—
ZnPcCl	$200 \pm 20$	—	$520 \pm 60$	—
CoPcCl	$14,7 \pm 0,4$	$85 \pm 8$	$98 \pm 11$	$415 \pm 29$
NiPcCl	$2,50 \pm 0,05$	—	$50 \pm 4$	—
PdPcCl	—	—	$13,3 \pm 0,6$	$27,5 \pm 0,5$
AlPcCl	—	—	—	$123 \pm 13$

Tables 4-6 present the values of  $k_{exp}$ , by the use of Brand's equation [18], these values can be used to find  $k_t$ , which is not dependent on H<sub>2</sub>SO<sub>4</sub> concentration. The high order of the reaction with respect to  $[H_3O^+]$ , which is

also characteristic of the cleavage of the etioporphyrins in  $H_2SO_4$  [10], indicates a complex mechanism for the hydrolysis of  $H_2PcH^+$ . A study of the mechanism of the hydrolysis of stable metal phthalocyanines, using the least stable  $(H_2SO_4)_2SnPc$  (Table 6), showed that they also obey Eq. (1), but the limiting step in hydrolysis is cleavage of the metal (2a), which takes place with the rupture of four metal-nitrogen coordination bonds so that  $k_{exp} = k_t [H_3O^+]^2$ . Stable phthalocyanines are appreciably hydrolyzed only at high temperatures (Table 5). The metals can be arranged in the following order of decreasing ease of cleavage of the central ion in phthalocyanines:

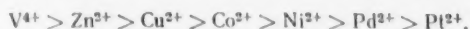


TABLE 6. Dependence of the Hydrolysis Rate Constant of  $Cl_2SnPc$  at 40° on  $H_2SO_4$  Concentration

$H_2SO_4$ , m/liter	$k_{exp} \cdot \text{hours}^{-1}$	$H_2SO_4$ , m/liter	$k_{exp} \cdot \text{hours}^{-1}$	$H_2SO_4$ , m/liter	$k_{exp} \cdot \text{hours}^{-1}$
14.10	$0.328 \pm 0.035$	16.05	$0.287 \pm 0.025$	17.25	$0.102 \pm 0.005$
15.08	$0.326 \pm 0.018$	17.00	$0.160 \pm 0.008$	17.70	$0.063 \pm 0.004$

In the series, listed before Table 6, the ions are arranged in the order of strengthening of the M-N bonds, which is accompanied by increasing neutralization of the basic properties of the intracyclic nitrogen atoms [11]. The basic properties are responsible for reactions (2) and (2a). The  $Pt^{2+}$  phthalocyanine is the most stable, and  $(H_2SO_4)AlPc$  has an extremely high stability. The series presented above, as far as it goes, is identical to the series for the stability of metal bonds in porphyrin complexes:  $Ba^{2+} > Mg^{2+} > Mn^{2+} > Fe^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Pd^{2+}$ , which was established from the shift  $\lambda_{max}$  in absorption spectra [7] and by the rate of cleavage of the metal [10]. This circumstance is a weighty argument in support of the proposition that in a series of monotypic complexes, the rate of cleavage of the central ion during attack by a proton can serve as a reliable method for characterizing the stability of the bonds of the metal with the ligand.

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# REACTIONS OF POLYFLUORINATED NITROSOALKANES WITH AMINES

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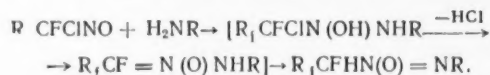
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Polyfluorinated nitrosoalkanes are compounds with clearly expressed electrophilic properties [1]. We present below a report of an investigation of the reactions of polyfluorinated nitrosocompounds with substances containing the nucleophilic  $\text{NH}_2$  group. Polyfluorinated nitrosoalkanes vigorously react with amines in an ether or alcoholic medium, forming resinous products. The corresponding azo compounds are obtained at low temperatures ( $-70$  to  $-100^\circ$ ) or in the presence of  $\text{CH}_3\text{COOH}$ :  $\text{R}_f\text{NO} + \text{H}_2\text{NR} \rightarrow [\text{R}_f\text{N}(\text{OH})\text{NHR}] \rightarrow \text{H}_2\text{O} + \text{R}_f\text{N}=\text{NR}$ .

Aliphatic, alicyclic, and aromatic primary amines react in accordance with the above. The activity of the amine decreases with a decrease in basicity. Thus, the rate of the reaction of aniline with trifluoronitrosomethane is lower than the reaction rate of aliphatic amines by more than three orders of magnitude. Amides and urethans do not react with nitroso compounds.

The mechanism of this reaction is graphically illustrated by the interaction of primary amines with polyfluoro-nitrosoalkanes containing a chlorine atom attached to the carbon bonded to the nitroso group. In this case, when the reaction is carried out at  $-50$  to  $-30^\circ$ ,  $\alpha$ -H-containing polyfluorinated azoxy compounds are formed in addition to the azo compounds. In reactions with amine carbonates, azoxy compounds are the major products.

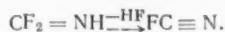


Thus, either the elements of water or  $\text{HX}$  may be eliminated from the primary product of the addition of an amine to a nitroso compound, azo compounds or azoxy compounds, respectively, being formed. Organic derivatives of hydrazine react with polyfluorinated nitroso compounds in a manner similar to that of primary amines:



and O-alkylhydroxylamines also react similarly:  $\text{R}_f\text{NO} + \text{H}_2\text{NOR} \rightarrow \text{R}_f\text{N}=\text{NOR}$ .

The properties of polyfluorotriazene, which is formed during the reaction of trifluoronitrosomethane with phenylhydrazine, are interesting. This substance undergoes fission under the influence of phenol with the formation of difluoroformine:  $[\text{C}_6\text{H}_5\text{NHN}=\text{NCF}_3] \rightarrow \text{C}_6\text{H}_5\text{N}=\text{NNHCF}_3 \xrightarrow{\text{C}_6\text{H}_5\text{OH}} \text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_4\text{OH} + [\text{CF}_3\text{NH}_2] \rightarrow \text{HF} + \text{CF}_2=\text{NH}$ . The latter pyrolyzes at  $420$ – $450^\circ$  (under vacuum over  $\text{NaF}$ ) to cyanogen fluoride:



The structure of the cyanogen fluoride was unequivocally proved both by conversion of the material to cyanuric fluoride and by other reactions (it hydrolyzed with the formation of  $\text{HF}$  and  $\text{HOCN}$ , reacted with aniline to form  $\text{N,N}'$ -diphenylguanidine, and with potassium sulfite to form potassium thiocyanate, etc.). Numerous attempts to synthesize this compound have been unsuccessful [2-7], and the data presented in the paper of Cosslett [2] on the properties of

TABLE 1. Newly Synthesized Compounds

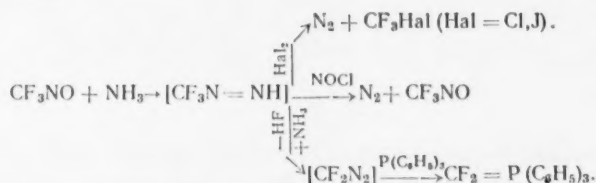
Compound	B.p., °C/mm	M.p., °C/mm	$d_{20}^{20}$	$n_D^{20}$	Found, %				Calculated, %					
					C	H	N	F	Cl	C	H	N	F	Cl
$CF_3N = NC_6H_5$	27.5	—	1.072	—	27.95	4.68	22.80	44.3	—	28.20	3.98	22.30	45.23	—
$CF_3N = NC_6H_4$	52	—	1.037	1.3193	27.24	4.77	20.15	40.32	—	34.30	5.00	20.0	40.71	—
$CF_3N = NC_6H_3$	77	—	1.015	1.3375	35.10	4.72	20.05	40.87	—	38.96	5.84	18.18	37.01	—
$CF_3N = NC_6H_{11}$	52/42	—	1.100	1.3870	34.90	5.10	18.30	36.95	—	—	—	15.55	31.66	—
$CF_3N = N<\text{C}_6\text{H}_4>$	141/752	—	1.222	1.4660	38.88	5.58	15.06	30.84	—	48.20	2.88	16.10	32.40	—
$CF_3N = N<\text{C}_6\text{H}_4>$	—	—	—	—	—	—	14.75	30.32	—	—	—	—	—	—
$CF_3N = NC_6H_4NO_2$ (ortho)	111/16	28	—	—	45.05	2.91	16.79	31.59	—	—	—	—	26.40	—
$CF_3N = NC_6H_4NO_2$ (para)	62	—	—	—	—	—	—	26.25	—	38.4	1.83	19.17	26.02	—
$CF_3N = NC_6H_4NO_2$ (meta)	104/2	—	1.440	1.5035	38.96	2.31	18.20	25.74	—	38.4	1.83	19.17	26.02	—
$CF_3N = NC_6H_4CH_3$ (ortho)	56/16	—	1.194	1.4747	40.33	2.31	18.70	26.56	—	50.8	3.72	14.9	30.4	—
$CF_3N = NC_6H_4CH_3$ (para)	82/50	—	1.196	1.4450	50.82	4.3	16.07	28.94	—	50.8	3.72	14.9	30.4	—
$CF_3N = NC_6H_4CH_3$ (meta)	68/30	—	1.187	1.4625	51.20	3.74	15.50	30.50	—	50.8	3.72	14.9	30.4	—
$CF_3N = NC_6H_4OCH_3$ (ortho)	76/4	17	1.292	1.5125	51.44	3.81	14.10	29.92	—	50.8	3.72	14.9	30.4	—
$CF_3N = NC_6H_4OCH_3$ (para)	53/3	29	—	—	90.97	3.44	14.53	30.17	—	47.59	3.42	13.73	27.94	—
$CF_3N = N<\text{C}_6\text{H}_4>COOH$	—	215	—	—	47.76	4.30	13.94	27.64	—	47.59	3.42	13.73	27.94	—
$CF_3N = N<\text{C}_6\text{H}_4>NH_2$	—	123	—	—	48.20	3.85	13.60	27.65	—	44.0	2.28	12.8	26.1	—
$CF_3N = N<\text{C}_6\text{H}_4>N =$ $= NCF_3$	194	—	—	—	47.70	4.05	14.28	28.35	—	58.9	3.77	15.85	21.42	—
$CF_3N = NCH_2CH_2N = NCF_3$	99	—	1.328	1.3226	43.56	2.50	11.32	25.75	—	48.4	2.30	16.20	33.20	—
$O_2NCF_2CF_2N = NCH_3$	36/100	—	1.416	1.3850	43.66	2.46	11.42	25.80	—	21.65	1.80	25.23	46.85	—
$O_2NCF_2CF_2N = NC_6H_5$	51/100	—	1.321	1.3470	59.54	5.07	15.80	22.44	—	18.9	1.58	22.0	40.0	—
$O_2NCF_2CF_2N = NC_6H_5$	85/1	—	1.331	1.3825	49.73	4.56	15.83	34.93	—	23.6	2.4	20.6	37.4	—
$ClCF_2CF_2N = NCH_3$	62	—	1.319	1.3310	49.73	3.00	16.70	34.93	—	38.20	2.20	16.70	30.2	—
$ClCF_2CF_2N = NC_6H_5$	59/4	—	1.356	1.4700	49.38	2.70	15.67	46.74	—	20.10	1.68	15.70	42.60	19.90
$BrCF_2CF_2N = NCH_3$	31/100	—	1.615	1.3600	21.82	1.92	25.42	46.67	—	30.90	2.07	11.20	31.50	14.7
					21.54	2.05	24.93	46.67	—	16.40	1.40	12.50	34.10	—
					18.97	2.05	21.80	38.50	—	—	—	—	—	—
					19.27	2.38	21.80	38.50	—	—	—	—	—	—
					23.40	2.38	19.20	38.16	—	—	—	—	—	—
					22.11	2.38	19.20	38.16	—	—	—	—	—	—
					38.13	2.28	17.68	29.11	—	—	—	—	—	—
					38.20	2.56	17.68	29.11	—	—	—	—	—	—
					21.29	2.42	15.34	41.62	—	17.80	1.83	17.83	42.60	19.90
					21.29	2.28	15.20	41.76	—	30.90	2.07	11.20	31.50	14.7
					50.83	1.88	11.68	20.57	—	14.60	1.40	12.50	34.10	—
					40.55	1.67	11.67	20.62	—	16.40	1.40	12.50	34.10	—
					16.47	1.54	12.20	33.72	—	—	—	—	—	—
					16.45	1.83	12.45	33.91	—	—	—	—	—	—

$\text{ClCF}_2\text{CHFN} = \text{NCH}_3$	47.5°/150	1.327	1.3620	23.07	3.18	16.57	35.30	21.80	22.40	2.50	17.40	35.60	22.01
$\text{NO}_2\text{CF}_2\text{CFN} = \text{NCH}_3$	45°/35	1.410	1.3840	23.38	3.21	16.54	35.46	22.06	17.5	1.40	20.5	27.80	17.3
$\text{ClCF}_2\text{CFN} = \text{NCH}_3$	53°/200	1.461	—	18.72	2.53	19.89	25.78	16.74	18.5	1.53	14.3	29.2	36.4
$\text{ClCF}_2\text{CFN} = \text{NC}_2\text{H}_5$	59.5°/100	1.333	—	18.57	0.97	14.13	25.02	38.06	22.90	2.38	13.40	28.30	3.04
$\text{ClCF}_2\text{CFN} = \text{NC}_4\text{H}_9$	75°/1	1.407	1.5030	23.16	1.15	13.32	27.96	34.76	37.40	1.90	10.90	22.20	27.60
$\text{BrCF}_2\text{CFN} = \text{NCH}_3$	59°/100	1.713	1.4035	23.36	1.26	13.57	27.90	34.67	15.05	1.25	11.60	23.82	—
$\text{NO}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{N} = \text{NC}_6\text{H}_5$	105°/30	1.473	1.4490	23.36	1.53	10.85	21.18	25.29	—	—	—	—	—
$\text{CF}_3\text{CIN} = \text{NCH}_3$	44	1.871	—	23.32	2.57	14.32	38.10	—	38.9	1.70	13.9	37.9	—
$\text{NO}_2\text{CF}_2\text{CFN}(\text{O})\text{NCH}_3$	65°/35	1.484	1.3980	19.39	2.92	20.70	28.73	25.19	18.70	2.33	21.80	29.50	27.60
$\text{ClCF}_2\text{CFN}(\text{O})\text{NCH}_3$	67°/100	1.450	1.3880	20.20	2.44	21.18	28.72	25.25	19.20	2.50	22.40	30.50	—
$\text{CF}_3\text{N} = \text{N} - \text{NHC}_2\text{H}_5$	—	—	—	20.81	2.10	15.39	32.48	21.36	20.40	2.30	15.90	32.40	20.10
$\text{CF}_3\text{N} = \text{N} - \text{N}(\text{C}_2\text{H}_5)_2$	117—119°/1	—	—	20.05	1.80	15.32	32.78	21.51	44.50	3.18	22.20	31.80	—
$\text{CF}_3\text{N} = \text{N} - \text{NHCOCH}_3$	—	—	—	20.81	2.10	15.39	32.48	21.36	59.0	3.80	15.80	21.50	—
$\text{CF}_3\text{N} = \text{N} - \text{NOCH}_3$	22—23°/60	1.452	—	24.49	3.13	20.53	46.43	—	23.20	2.60	27.10	36.80	—
$\text{CF}_3\text{OCH}_3$	—22.5°/746	—	—	23.28	2.68	46.53	—	—	24.00	3.00	—	57.00	—
$\text{CF}_3\text{OC}_2\text{H}_5$	5.5—6°/753	—	—	23.74	3.05	57.32	—	—	—	—	—	50.00	—
$\text{CF}_2 = \text{NH}$	—22°/80	—	—	—	—	49.50	—	—	18.50	—	—	58.50	—
$\text{FC} = \text{N}^*$	—47	—	—	18.36	—	59.26	—	—	—	—	—	42.22	—
$\text{CF}_3\text{N}_3$	—28.5°/743	—	—	—	—	39.90	—	—	—	—	—	51.35	—
$\text{CF}_2\text{HONO}$	2°/2	1.388	1.3288	12.99	3.13	37.80	51.12	—	10.81	—	37.83	39.17	—
$\text{CF}_2\text{HONO}^{**}$	—20	—	—	12.84	3.24	37.80	51.12	—	12.40	1.04	14.60	39.17	—
$(\text{CF}_2\text{H})_2\text{NONO}$	+9	—	—	—	—	11.33	35.70	—	—	—	14.30	39.20	—
		—	—	14.88	1.40	16.52	46.75	—	14.80	1.23	17.30	46.85	—

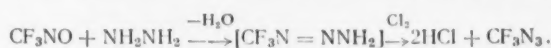
\* Mol. wt.: found, 46.92, 45.94; calculated, 45.0. During storage for three days at  $-70^\circ$ , the substance transformed to cyanuric fluoride; b.p. +72–72.5°;  $d = 1.5720$ ; analysis: C, 27.78%; F, 41.75% (calc.: C, 26.66%; F, 42.2%). It hydrolyzed to  $\text{C}_3\text{H}_3\text{O}_3\text{N}_3$ . Analysis: C, 28.41, 28.60%; H, 1.91, 2.20%; N, 31.97, 32.30% (Calculated: C, 27.9%; H, 2.30%; N, 32.51%). The reaction with aniline gave N,N-diphenylguanidine with an m.p. of 147°.

\*\* Mol. wt.: found, 100.0, 95.0; calc., 97.0.

cyanogen fluoride have been shown to be erroneous.\* The reaction of trifluoronitrosomethane with ammonia at  $-70^\circ$  in alcoholic or ether medium gave the relatively unstable trifluoromethyldiimide, the presence of which in the solution was proved by the reactions:



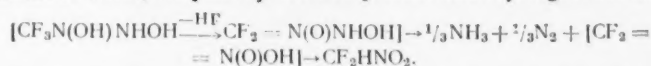
Trifluoronitrosomethane reacts with aqueous ammonia with the formation of nitrogen and fluoroform:  $\text{CF}_3\text{NO} + \text{NH}_3 \rightarrow [\text{CF}_3\text{N}=\text{NH}] \rightarrow \text{N}_2 + \text{CF}_3\text{H}$ . The reaction of trifluoronitrosomethane with aqueous methylamine gives a quantitative yield of trifluoroazomethane. The interaction of trifluoronitrosomethane with hydrazine under ordinary conditions converts the nitroso compound to inorganic compounds. At low temperatures ( $-70^\circ$ ) in a methanol medium, an unstable triazene is formed, and this is converted by chlorine to trifluoromethyl azide:



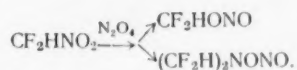
The reaction of trifluoronitrosomethane with hydroxylamine at low temperature takes place similarly; trifluoromethyl diazohydroxide is formed, and this is converted in alcoholic media to the corresponding trifluoromethyl ether:



In alcoholic alkali, the reaction between trifluoromethylnitrosomethane and hydroxylamine follows a different course; instead of losing the elements of water, the primary addition product loses hydrogen fluoride and is converted to difluoronitromethane:



Difluoronitromethane reacts with nitrogen oxides in carbon tetrachloride at  $0^\circ$  to form difluoromethyl nitrite and  $\text{N}_1\text{,N-bis(difluoromethyl)hydroxylamine nitrite}$ :



It is apparent from our report that the nitroso group in polyfluorinated nitrosoalkanes behaves similarly to the nitroso group in aromatic compounds in many condensation reactions with substances containing an  $\text{NH}_2$  group. This is evidently a consequence of the strongly electrophilic action of polyfluorinated radicals (cf. [9-14]).

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\* In 1960, after completion of the present investigation, a paper [8] appeared reporting that the pyrolysis of cyanuric fluoride at  $1300^\circ$  under vacuum gives cyanogen fluoride; the constants of this compound were in agreement with our

PYRROLIZIDINE ALKALOIDS. THE ABSOLUTE CONFIGURATION  
OF 1-METHYLENEPYRROLIZIDINE AND OTHER PYRROLIZIDINE  
BASES

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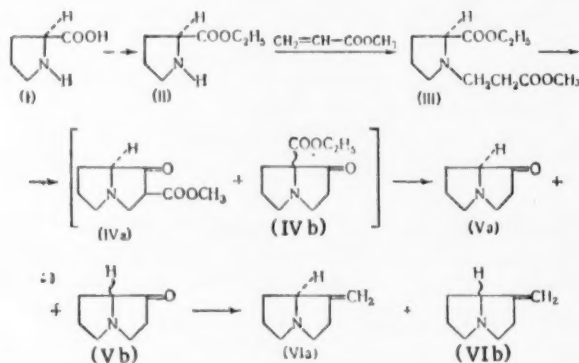
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We have recently described the total synthesis of the alkaloid 1-methylenepyrrolizidine [1], which was first isolated by Culvenor and Smith [2] from the perennial shrub *Crotalaria anagyroides* H. B. and K. In the present article, we describe the stereospecific synthesis of this alkaloid, which makes it possible to establish its absolute configuration as well as the absolute configurations of the natural pyrrolizidine bases associated with it. The synthesis was carried out by the scheme previously described for the synthesis of racemic 1-methylenepyrrolizidine:



The starting material was the ethyl ester of L-proline (II), which was prepared by esterification of natural proline (I). Condensation of II with methyl acrylate gave the methyl ester of  $\beta$ -(N-2-carbethoxypyrrolidine)propionic acid, which was then subjected to Dieckmann condensation. Two keto esters (IVa and IVb) could be formed during the cyclization, but only one ketone is obtained from them by ketonic cleavage. We did not separate the mixture of keto esters into the individual compounds. They were converted to 1-oxopyrrolizidine by heating with 10% hydrochloric acid. Had the condensation proceeded with the formation of only IVa, optically pure Va should have been obtained; on the contrary, had the condensation led only to IVb, racemic Vb would have been formed, and, finally, had both IVa and IVb been formed in the condensation, partially racemized 1-oxopyrrolizidine (a mixture of Va and Vb) would have been formed. In the actual case, the 1-oxopyrrolizidine had the rotation  $c [\alpha]_D^{21} -22.4^\circ$  (C, 1.25; ethanol), but we had no opportunity to compare this rotation with that of the optically pure substance.

It should also be mentioned that, in contrast to the usual  $\alpha$ -ketoamines, Va is quite stable with respect to racemization. When it was stored for a day at a temperature of about  $-30^\circ$  and subsequently redistilled, the angle of rotation was not significantly changed, although 1-oxopyrrolizidine itself is a relatively labile compound. The comparative stability of 1-oxopyrrolizidine toward racemization is probably associated with the fact that the formation of the enamine form, which is required for racemization, is energetically unfavorable owing to lack of coplanarity of the pyrrolizidine system.



The 1-oxopyrrolizidine was converted by Wittig reaction [3] to 1-methylenepyrrolizidine, which had  $[\alpha]_D^{20} -33^\circ$  (C, 1.02; ethanol) (natural 1-methylenepyrrolizidine has  $[\alpha]_D^{20} 43.1^\circ$ ). The i.r. spectrum of this substance was completely identical to that of the natural alkaloid.

These data unequivocally indicate that the absolute configuration of 1-methylenepyrrolizidine corresponds to the absolute configuration of L-proline. This result is in agreement with the present concept of the biogenesis of pyrrolizidine bases, which is associated with conversions of amino acids. The difference between the angle of rotation of the synthetic product and that of the natural alkaloid indicates that the Dieckmann condensation yields both possible keto esters, IVa and IVb, in an approximate ratio of 3:1 (this does not take into account possible racemizations during the course of this and further conversions).

Since we carried out the synthesis of natural 1-methylenepyrrolizidine from natural proline, which has an S configuration)\*, it has been shown that the alkaloid is (7S)-1-methylenepyrrolizidine, i.e., it has the structure VIa, which agrees completely with the data of Culvenor and Smith [2].

Since, as has previously been shown [2], hydrogenation of 1-methylenepyrrolizidine results in heliotridane and pseudoheliotridane, and since the relative configuration of the pyrrolizidine bases is well known [5], it can be concluded that heliotridane is (1S, 7S)-1-methylenepyrrolizidine, and its epimer, pseudoheliotridane, is (1R, 7S)-1-methylenepyrrolizidine. With a knowledge of the absolute configuration of these bases, it is easy to establish the absolute configuration of all remaining natural pyrrolizidine bases.

These conclusions, which were formed on the basis of the direct stereospecific synthesis of 1-methylenepyrrolizidine, are in complete agreement with the data of Warren and Klemperer [6], which were obtained during a study of the products of the degradation of natural pyrrolizidine bases; they are also in agreement with the conclusions of Adams [7].

#### EXPERIMENTAL

**Ethyl ester of L-proline (II).** A mixture of 4.5 g of L-proline and 46 ml of absolute alcohol was cooled to  $0^\circ$ , and 3.4 ml of thionyl chloride was added dropwise to the well-stirred mixture. The reaction mixture was allowed to stand at room temperature for 48 hours. The alcohol was distilled. The residue was dissolved in 30 ml of dry chloroform, and 35 ml of dry chloroform saturated with ammonia was added at a temperature not exceeding  $0^\circ$ . The mixture was allowed to stand for half an hour, and the precipitate was removed by filtration. The chloroform was distilled at a temperature not above  $20^\circ$ , and the residue was distilled under vacuum, the fraction boiling at  $40^\circ/2$  mm being collected. The yield was 5 g (89%);  $n_D^{20}$  1.4496. Literature data [8]: b.p.,  $78^\circ/12-14$  mm.

**Methyl ester of L- $\beta$ -(N-2-carbethoxypyrrolidine) propionic acid (III).** A mixture of 4.84 g of the ethyl ester of L-proline and 9 ml of methyl acrylate, containing a trace of hydroquinone, was refluxed for 24 hours. The excess methyl acrylate was distilled. The residue was distilled under vacuum, and the fraction boiling at  $98-100^\circ/1-1.5$  mm was collected. The yield was 6.5 g (83%);  $d_4^{20}$  1.0823,  $n_D^{20}$  1.4564;  $[\alpha]_D^{22} -66.5^\circ$  (pure liquid);  $[\alpha]_D^{22} -72^\circ$  (C, 3.49; ethanol). Found %: C 57.36; 57.39; H 8.35; 8.48; N 6.02; 6.14.  $C_{11}H_{19}O_4N$ . Calculated %: C 57.58; H 8.39; N 6.11.

**1-Oxopyrrolizidine (V).** To alcohol-free sodium ethylate (from 0.53 g of metallic sodium) was added 1.3 ml of absolute alcohol, 40 ml of absolute xylene, and 5 g of the methyl ester of L- $\beta$ -(N-2-carbethoxypyrrolidine) propionic acid (III). The reaction mixture was heated on an oil bath ( $150-160^\circ$ ) for 1.5 hours. After cooling, the reaction product was extracted with water (four portions of 15 ml each). To the combined aqueous extracts was added 40 ml of concentrated hydrochloric acid, and the resulting solution was heated on a boiling water bath for 3 hours. The reaction mixture was evaporated, and the residue was dissolved in 10 ml of water. The solution was saturated with potassium carbonate as it was cooling and then carefully extracted with ether. After distillation of the ether, the product was concentrated by boiling with dry benzene, and was then distilled by vacuum distillation under an atmosphere of nitrogen. The 1-oxopyrrolizidine was obtained as a colorless oily liquid, which darkened rapidly in air. B.p.,  $56-58^\circ/3$  mm; yield, 1.4 g (51%, calculated on the III);  $n_D^{20}$  1.4867,  $[\alpha]_D^{21} -45^\circ$  (pure liquid);  $[\alpha]_D^{21} -22.4^\circ$  (C, 1.25; ethanol). After storage for a day at temperature of about  $-30^\circ$  and redistillation, the rotation was  $[\alpha]_D^{21} -21^\circ$  (C, 1.25; ethanol). Found %: N 11.09; 11.42.  $C_7H_{11}ON$ . Calculated %: N 11.19.

**1-Methylenepyrrolizidine (VI).** To a solution of 1.22 g of sodium amide in 200 ml of liquid ammonia was added 11.2 g of triphenylmethylphosphonium bromide. The ammonia was displaced with absolute ether (200 ml),

\* The notation used for the absolute location of atoms at an asymmetric carbon atom is that of reference [4].

and the resulting mixture was refluxed for 30 minutes. To the cooled ether solution of methylenetriphenylphosphorane was added a solution of 1.4 g of 1-oxopyrrolizidine in 30 ml of absolute ether. The reaction mixture was refluxed for 2 hours and allowed to stand at room temperature for 2 days. The resulting mixture was evaporated with ether, and the ether solution was dried with magnesium sulfate. The ether was distilled, and the residue was distilled under vacuum, the fraction boiling at 111-113/172 mm being collected. The yield was 0.72 g;  $n_D^{20}$  1.4884,  $[\alpha]_D^{25}$  -33° (C, 1.02; ethanol). Found %: C 77.80; 77.51; H 10.66; 10.34; N 11.34; 11.63.  $C_9H_{13}N$ . Calculated %: C 77.99; H 10.64; N 11.37. Literature data [2]: b.p., 120°/170 mm;  $[\alpha]_D^{20}$  -43.1° (C, 1.07; ethanol).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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## SCANDIUM CHALCOGENIDES

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Except for the oxide, none of the scandium chalcogenides have been studied. The only information in the literature relates to the preparation of scandium sesquisulfide,  $\text{Sc}_2\text{S}_3$  [1], and scandium sesquiselenide,  $\text{Sc}_2\text{Se}_3$  [2]. We have previously described methods for the preparation and the crystal structures of scandium sesquiselenide ( $\text{Sc}_2\text{Se}_3$ ) and scandium sesquitelluride ( $\text{Sc}_2\text{Te}_3$ ) [3]. In addition to  $\text{Sc}_2\text{Te}_3$ , the Se-Te system also contains a compound of the composition  $\text{ScTe}$ , which is characterized by its own set of interplanar distances.

The present article presents the results of an x-ray investigation of  $\text{Sc}_2\text{O}_3$ ,  $\text{Sc}_2\text{S}_3$ , and the scandium telluride of the composition  $\text{ScTe}$ . Individual compounds having a 1:1 ratio of the elements were not observed in the systems Sc-S and Sc-Se. Scandium oxide having a purity of more than 99.9% was used in the investigation. This was prepared from the technical oxide by thiocyanate extraction and precipitation of scandium oxalate [4].  $\text{Sc}_2\text{S}_3$  and  $\text{ScTe}$  were synthesized from the elements. Metallic scandium having a purity of 97-97.5% was prepared by reduction of anhydrous scandium chloride with metallic calcium [5]. Selenium-free sulfur was preliminarily remelted and purified by vacuum sublimation ( $10^{-4}$ - $10^{-5}$  mm Hg) at 100-110°C. The purity of the sublimed sulfur was greater than 99.9%. Tellurium having a purity greater than 99.99% was prepared from the technical product by twice reprecipitating tellurium dioxide [6], reduction of the oxide, remelting of the elemental tellurium, and vacuum sublimation ( $10^{-4}$ - $10^{-5}$  mm Hg) at 400° [7].

Synthesis of the  $\text{Sc}_2\text{S}_3$  and  $\text{ScTe}$  was carried out as follows. Equivalent amounts of metallic scandium and the appropriate chalcogen were mixed well and placed in a quartz ampoule having a volume of about 10 ml. The ampoule was then pumped to  $10^{-4}$  mm Hg and sealed. Each mixture weighed 3-5 g. Synthesis and annealing times were:

$\text{Sc}_2\text{S}_3$		$\text{ScTe}$	
Temp., °C	Heating time, hours	Temp., °C	Heating time, hours
20-120	4	20-400	1
120-150	6	400	4
150-450	6	400-500	6
450	2	500-1000	1
450-1000	1	1000	6
1000	6		

The  $\text{Sc}_2\text{S}_3$  and  $\text{ScTe}$  were infusible crystalline powders having, respectively, a yellow and a green color.

X-ray powder photographs of  $\text{Sc}_2\text{O}_3$ ,  $\text{Sc}_2\text{S}_3$ , and  $\text{ScTe}$  were taken with filtered  $\text{CuK}_\alpha$  radiation using RKD-57 and RKU-86 cameras. The intensities of the lines were estimated visually on a five-point scale. Results of the x-ray analyses are presented in Tables 1, 2, and 3.

All lines on the scandium oxide pattern were satisfactorily indexed for a body-centered cubic lattice of the  $\text{Mn}_2\text{O}_3$  type [8] with  $a=9.835 \pm 0.005$  kX and  $Z=16$ . The literature [9-11] reports a somewhat lower lattice parameter for the  $\text{Sc}_2\text{O}_3$  lattice—from 9.76 to 9.828 kX (see Table 4). The x-ray density of the scandium oxide was 3.84 g/cc, while the pycnometric value was 3.75 g/cc.

The intensities of the lines on the scandium sulfide pattern were sharply divided into two categories, very weak and strong. The strong lines were indexed as a primitive cubic lattice with  $a_0=2.591$  kX, which represents a subcell.

The weak lines were due to a superstructure. By analogy with the recently established structure of  $\beta\text{-In}_2\text{S}_3$  [12], we propose for  $\text{Sc}_2\text{S}_3$  a face-centered tetragonal lattice with  $a = 10.37 \pm 0.01$  kX ( $a = a_0 \times 4$ ) and  $c = 31.11 \pm 0.03$  kX;  $c/a = 3$ ,  $Z = 32$ . Actually, of the 24 weak lines up to  $\theta \approx 40^\circ$ , 21 lines were satisfactorily indexed in this tetragonal lattice. The presence of unindexed lines can be explained by the existence of some superstructure in the scandium sulfide or by the presence of very small amounts of foreign material. The x-ray density calculated for this tetragonal lattice was 2.96 g/cc, while the pycnometric density of  $\text{Sc}_2\text{S}_3$  determined with chloroform, was 2.80 g/cc; the literature reports a density of 2.85 g/cc [1].

TABLE 1. Results of the X-Ray Analysis of Scandium Oxide

Line no.	Intensity	hkl	Interplanar distance, d, kX		a, kX, found	Line no.	Intensity	hkl	Interplanar distance, d, kX		a, kX, found
			found	calculated for $a = 9.835$ kX					found	calc. for $a = 9.835$ kX	
1	3	211	4.014	4.015	9.833	30	2	844	1.004	1.004	9.835
2	5	222	2.835	2.839	9.822	31	1	941; 853; 770	0.9934	0.9936	9.833
3	2	400	2.456	2.450	9.827	32	1	860; 10, 0, 0	0.9831	0.9836	9.831
4	2	332	2.094	2.097	9.822	33	2	862; 10, 2, 0	0.9641	0.9645	9.831
5	1	521	1.793	1.795	9.822	34	1	666; 10, 2, 2	0.9465	0.9465	9.835
6	5	440	1.736	1.739	9.822	35	1	952; 10, 3, 1; 765	0.9376	0.9378	9.833
7	1	530; 433	1.687	1.687	9.835	36	1	871; 855; 774	0.9209	0.9213	9.831
8	2	532; 611	1.595	1.596	9.834	37	1	864; 10, 4, 0	0.9135	0.9133	9.838
9	1	620	1.554	1.555	9.829	38	1	961; 10, 3, 3	0.9053	0.9055	9.833
10	3	541	1.516	1.518	9.824	39	1	10, 4, 2	0.8976	0.8978	9.833
11	3	622	1.481	1.483	9.822	40	1	11, 1, 0; 954; 873	0.8902	0.8904	9.833
12	2	631	1.451	1.450	9.840	41	2	10, 5, 1; 11, 2, 1; 963	0.8766	0.8762	9.840
13	1	444	1.418	1.420	9.825	42	1	882; 10, 4, 4	0.8559	0.8561	9.833
14	1	710; 550; 543	1.389	1.391	9.825	43	1	10, 5, 3; 11, 3, 2; 972; 776	0.8502	0.8498	9.840
15	1	640	1.362	1.364	9.822	44	1	866; 10, 6, 0	0.8437	0.8433	9.840
16	1	721; 633; 552	1.338	1.338	9.835	45	1	875; 11, 4, 1	0.8377	0.8373	9.840
17	1	642	1.315	1.314	9.840	46	1	10, 6, 2	0.8310	0.8312	9.833
18	1	732; 651	1.250	1.249	9.840	47	1	884; 12, 0, 0	0.8198	0.8196	9.838
19	1	800	1.228	1.229	9.822	48	1	981; 12, 1, 1; 11, 5, 0; 11, 4, 3 974	0.8138	0.8140	9.833
20	1	741; 811; 554	1.211	1.211	9.835	49	1	12, 2, 0	0.8085	0.8085	9.835
21	1	820; 644	1.192	1.193	9.831	50	1	10, 7, 1; 11, 5, 2; 10, 5, 5	0.8030	0.8032	9.833
22	1	653	1.175	1.176	9.831	51	2	10, 6, 4; 12, 2, 2	0.7978	0.7978	9.835
23	1	660; 822	1.158	1.159	9.829	52	2	10, 7, 3; 11, 6, 1	0.7824	0.7825	9.933
24	1	831; 750; 743	1.143	1.143	9.835	53	2	12, 4, 0	0.7775	0.7775	9.835
25	2	662	1.128	1.128	9.835						
26	1	840	1.100	1.100	9.835						
27	1	921; 761; 655	1.061	1.061	9.835						
28	1	930; 851; 754	1.027	1.027	9.835						
29	1	763; 932	1.013	1.014	9.827						

$a_{cp} = 9.835 \pm 0.005$  kX

TABLE 2. Results of the X-Ray Analysis of Scandium Sulfide

Line no.	Intensity	hkl	Interplanar distance, d, kX		Line no.	Intensity	hkl	Interplanar distance, d, kX	
			found	calculated for $a = 10.37, c = 31.11$ kX				found	Calculated for $a = 10.37, c = 31.11$ kX
1	2	113?	5.83	5.99	15	5	440	1.833	1.833
2	1	115	4.78	4.75	16	1	519	1.761	1.753
3	2	222	3.57	3.57	17	1	3, 3, 13	1.711	1.710
4	1	208	3.11	3.11	18	2	4, 0, 14	1.686	1.687
5	1/2	226	3.00	2.99	19	1/2	622	1.629	1.630
6	5	400	2.60	2.59	20	1/2	3, 3, 15	1.581	1.581
7	1/2	402	2.555	2.557	21	1/2	*	1.528	—
8	1/2	2, 2, 10	2.370	2.372	22	5	4, 4, 12	1.497	1.497
9	1/2	424	2.217	2.222	23	1	1, 1, 21	1.451	1.452
10	1/2	*	2.182	—	24	1	644	1.413	1.414
11	1	2, 2, 12?	2.099	2.116	25	1/2	*	1.374	—
12	1	511	2.031	2.030	26	5	800	1.296	1.296
13	1	428	1.990	1.992	27	1/2	739	1.267	1.267
14	1	2, 2, 14	1.896	1.900	28	1/2	4, 0, 22	1.241	1.241

\* Origin of line not established.

All 25 lines on the ScTe pattern indexed well for a hexagonal lattice of the type of NiAs with  $a = 4.112 \pm 0.005$  kX,  $c = 6.735 \pm 0.005$  kX,  $c/a = 1.634$ ,  $Z = 2$ . The x-ray density of the ScTe was 5.75 g/cc, while the pycnometric density, determined with bromoform, was 5.65 g/cc.

TABLE 3. Results of the X-Ray Analysis of the Scandium Telluride of the Composition ScTe

Line no.	Intensity	hkl	Interplanar distance, d, kX		Line no.	Intensity	hkl	Interplanar distance, d, kX	
			found	calculated for $a=4.122, c=6.735$ kX				found	calculated for $a=4.122, c=6.735$ kX
1	1	002	3.38	3.37	14	1	212	1.253	1.253
2	5	101	3.167	3.155	15	1	204	1.226	1.225
3	4	102	2.458	2.450	16	2	300	1.189	1.190
4	4	110	2.660	2.661	17	2	213	1.156	1.156
5	3	103	1.903	1.900	18	1	302	1.121	1.122
6	2	112	1.757	1.758	19	2	205	1.075	1.075
7	2	201	1.728	1.726	20	1	220	1.031	1.031
8	1	004	1.683	1.683	21	1	222	0.9834	0.9854
9	2	202	1.580	1.577	22	1	311	0.9777	0.9796
10	2	203	1.399	1.397	23	1	304	0.9708	0.9717
11	2	211	1.323	1.323	24	2	206	0.9500	0.9502
12	2	144	1.303	1.304	25	1	313	0.9050	0.9059
13	2	105	1.261	1.260					

TABLE 4. Some Properties of the Scandium Chalcogenides

Compound	Color	Density, g/cc		Crystal lattice	Type of lattice	Z	Lattice parameters, kX
		pycno-metric	x-ray				
Sc <sub>2</sub> O <sub>3</sub>	White	3.70	3.84	Body-centered cubic	Mn <sub>2</sub> O <sub>3</sub>	16	$a = 9.76$ (9) $a = 9.79$ (10) $a = 9.825$ (11) $a = 9.835 \pm 0.005$
Sc <sub>2</sub> S <sub>3</sub>	Yellow	2.80	2.96	Face-centered tetragonal	$\beta$ -In <sub>2</sub> S <sub>3</sub>	32	$a = 10.37 \pm 0.01$ $c = 31.11 \pm 0.03$ $c/a = 3$
Sc <sub>2</sub> Se <sub>3</sub>	Brown-violet	4.51	4.55	Face-centered cubic	$\gamma'$ -Al <sub>2</sub> O <sub>3</sub>	11/3	$a = 5.405 \pm 0.005$
Sc <sub>2</sub> Te <sub>3</sub>	Black	5.26	5.32	Face-centered cubic	$\gamma'$ -Al <sub>2</sub> O <sub>3</sub>	11/3	$a = 5.805 \pm 0.005$
ScTe	Black	5.65	5.75	Hexagonal	NiAs	2	$a = 4.122 \pm 0.005$ $c = 6.735 \pm 0.005$ $c/a = 1.634$

Our results are not in good agreement with the data recently published in reference [13], in which it was reported that ScTe crystallizes in a hexagonal lattice with  $a = 6.728$  Å and  $c = 8.360$  Å. The type of crystal lattice Z and the density of the ScTe were not reported in this paper.

Properties of presently known scandium chalcogenides are presented in Table 4. It should be noted that the color of these compounds changes regularly from white to black in conformity with the increase in polarizability of the chalcogen, and the crystal lattices of all of the scandium chalcogenides are characterized by a high degree of symmetry.

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# INHIBITORS OF FREE RADICAL REACTIONS. AUTOALKYLATION OF 3,5-DI-*tert*-BUTYL-4-HYDROXYBENZYLAMINE

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It is well known that the preparation of substituted tribenzylamines is attended by certain difficulties, due chiefly to the formation of difficultly separable mixtures of primary, secondary, and tertiary amines when the usual methods are employed. The specific synthesis of individual amines is laborious and requires several stages. For this reason, the problem of the development of methods of synthesis which will yield individual products is important.

The present paper considers the autoalkylation of 3,5-di-*tert*-butyl-4-hydroxybenzyl amines, which, under mild conditions, results in the formation of the corresponding tribenzylamine in quantitative yield:

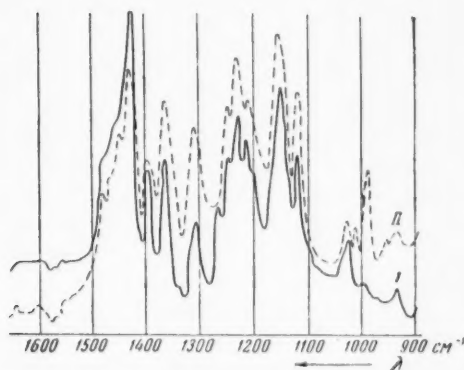
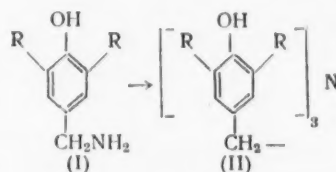


Fig. 1. I.r. spectra of tri(3,5-di-*tert*-butyl-4-hydroxybenzyl)-amine (II) and 2,6-di-*tert*-butyl-4-methylphenol (I).



In a study of the properties of 3,5-di-*tert*-butyl-4-hydroxybenzylamine [1], we found that tri-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-amine (II,  $\text{R} = \text{C}(\text{CH}_3)_3$ ) [1] is formed even when the primary amine is merely recrystallized from an azeotropic alcohol-water mixture. This reaction also takes place when an alcoholic solution of the amine (I,  $\text{R} = \text{C}(\text{CH}_3)_3$ ) is allowed to stand in an atmosphere of nitrogen at 20° for 2-3 days. The process is accelerated by an increase in the temperature and by an increase in the water content of the alcohol.

In order to clarify the effects of solvent and temperature on the nature of the reaction, a series of experiments was carried out (see Table 1). The same product, m.p. 231-231.5° (from nonane), was obtained in all cases.

I.r. and n.m.r. spectra of the resulting compound were recorded and the compound was synthesized by an alternate route with the aim of establishing the structure of the compound. The spectra of the tertiary amine (II,  $\text{R} = \text{C}(\text{CH}_3)_3$ ) were compared with spectra of model compounds in order to interpret the results. Tribenzylamine, 2,6-di-*tert*-butyl-4-methylphenol, and 2,6-di-*tert*-butylphenol served as model compounds.

When the i.r. spectrum of tri-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-amine (II,  $\text{R} = \text{C}(\text{CH}_3)_3$ ) (Fig. 1) is compared with that of 2,6-di-*tert*-butyl-4-methylphenol (I), it is found that a new band appeared in the 1010-1030  $\text{cm}^{-1}$  region of the spectrum of the amine. Examination of the n.m.r. spectra (Fig. 2) of the reaction product (II), 2,6-di-*tert*-butylphenol (3) and tribenzylamine (2) reveals the presence of a signal due to the protons of the  $\text{CH}_2$  groups in the first and third cases and the absence of such a signal in the second case. The ratio of the intensity of the signal of the phenyl protons to that of the protons of the  $\text{CH}_2$  group (1:1) indicates that they are present in equal amounts. This fact confirms the presence of benzyl radicals in the product.

It is interesting to note that the chemical shift of the signal of the hydroxyl proton of 2,6-disubstituted phenols is approximately equal to the chemical shift of the signal of the hydroxyl proton of the unsubstituted phenol (as extrapolated to infinite dilution in carbon tetrachloride solution) [2]. The shift of the signal of the hydroxyl proton in this region of the spectrum is the result of fission of hydrogen bonds.

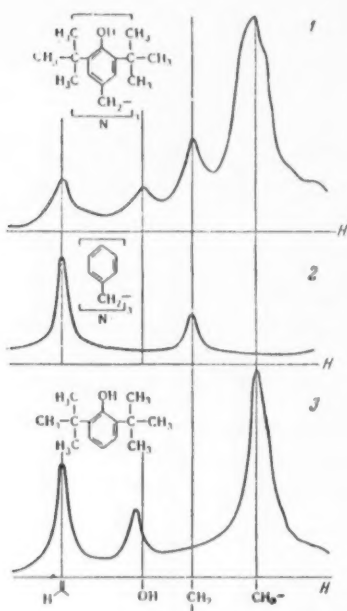


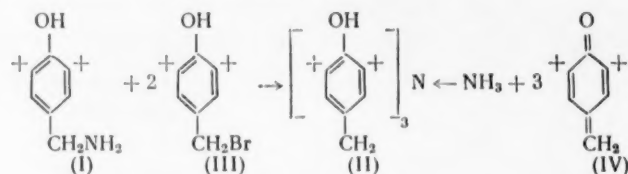
Fig. 2. N.m.r. spectra of tri-(3,5-di-tert-butyl-4-hydroxybenzyl)-amine, II (1), tribenzylamine (2), and 2,6-di-tert-butylphenol (3).

the corresponding benzyl bromide (III) [6]. Dry ammonia was passed through an ether solution of the methylenequinone (IV) for 2 hours. After removal of the ether, the residue was crystallized from nonane. M.p. 231–232°. A mixture of substituted tribenzylamine (II) with the autoalkylation product melted without depression of the melting point.

The decrease in the tendency toward a formation of hydrogen bonds or the complete absence of such a tendency apparently explains the increase in the inhibiting effect of phenols with the introduction of substituents into the ortho positions. The increase in the inhibiting activity in the series 2,6-dimethyl-, 2,6-diisopropyl-, and 2,6-di-tert-butyl-4-methylphenols [3] and the absence of a further increase for homologs with  $C_6$  to  $C_8$  substituents in the ortho positions [4] are understandable on the basis of the above.

Extension of this rule to other series of o,o-disubstituted phenols would probably permit confirmation of the hypothesis.

Synthesis of tri-(3,5-di-tert-butyl-4-hydroxybenzyl)-amine by an alternate route provided final proof of structure:



When 3 g of 3,5-di-tert-butyl-4-hydroxybenzyl bromide (III) [5] in 20 ml of dry benzene was added to a solution of 1.2 g of 3,5-di-tert-butyl-4-hydroxybenzylamine (I,  $R = C(CH_3)_3$ ) in 45 ml of dry pyridine, pyridine hydrobromide precipitated. The mixture was allowed to stand for a day at 20°. The precipitate was separated, the solvent was distilled under vacuum, and the residue was crystallized from nonane. The yield was 1.1 g; m.p. 231–232°. 2,6-Di-tert-butyl-4-methylene-2,5-cyclohexadienone (IV) was prepared from the

TABLE 1. Effect of Water Content of the Solvent and of Temperature on the Formation of Tri-(3,5-di-tert-butyl-4-hydroxybenzyl)-amine\*

Solvent	Water content, %	Reaction temp.	Reaction time, min.	M.p., °C
Ethyl alcohol	4	75–80	60	218–224
"	4	30–40	120	220–224
"	4	20	3 days	228–230
"	10	15–80	20	226–230
"	20	75–80	20	224–228
Dioxane	2	75–80	30	228–231
"	20	75–80	20	227–230
Pyridine	5	75–80	25	229–231
"	20	75–80	20	228–231

\* In all cases, after recrystallization from nonane, the compound melted at 231–232°; the yield after recrystallization was 83–90%.

On the basis of this study, the compound formed by autoalkylation of benzylamine was assigned the structure of tri-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-amine. Found %: C 80.28; 79.95; H 10.34; 10.37; N 1.93; 2.12.  $C_{45}H_{69}O_3$ . Calculated %: C 80.42; H 10.34; N 2.08.

Attempts to carry out the autoalkylation by prolonged refluxing in anhydrous organic solvents gave negative results. The solvents used were pyridine, higher alcohols, dioxane, and tetrahydrofuran. The original amine (I) was recovered after vacuum distillation of the solvent in a stream of nitrogen. It is apparent from Table 1 that the water content of the medium plays an important part in the autoalkylation process.

However, it should be noted that refluxing of the hydrochloride or the hydrobromide of amine (I) in 75% alcohol for 3 hours did not yield tri-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-amine.

Finally, the fact that amine I loses ammonia on standing forming tri-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-amine is deserving of attention. This process is also accelerated by an increase in temperature. This tribenzylamine (II,  $R = C(CH_3)_3$ ) is formed in quantitative yield when I is heated at 160-170° in a stream of nitrogen. The fact that benzylamine I ( $R = C(CH_3)_3$ ) is converted during melting to some "substance of obscure structure" was mentioned by Müller and co-workers [7].

A future communication will be devoted to a discussion of the mechanism of the process and of the extension of the process to substituted *p*-hydroxy-, *p*-alkoxy-, and *p*-acylhydroxybenzylamines.

The authors express their appreciation to Corresponding Member Acad. Sci. USSR, N. M. Emanuel for suggesting the problem and for constant interest in the work, and they also desire to thank T. N. Dyumaev and V. F. Bystronov for taking the i.r. and n.m.r. spectra. Our thanks are also due A. A. Volod'kina for the gift of the 2,6-di-*tert*-butylphenol.

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# THE DECOMPOSITION OF DIPHENYLMERCURY IN CYCLOHEXANE AND CYCLOHEXENE

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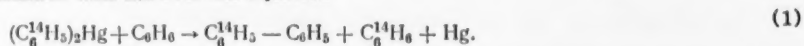
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Translated from Doklady Akademii Nauk SSSR, Vol. 141, No. 2,  
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We showed in earlier work [1] that the decomposition of diphenylmercury takes place in benzene with the participation of the benzene in accordance with the over-all equation



In this case, it was assumed that the reaction proceeds homolytically in the reaction complex. In connection with our study of free radical reactions it appeared of interest to determine the manner in which the decomposition of diphenylmercury takes place in nonaromatic solvents. We selected cyclohexane and cyclohexene as the nonaromatic solvents. Experiments were carried out on both the photodecomposition and the thermal decomposition of this compound.

The photodecomposition of  $(\text{C}_6\text{H}_5)_2\text{Hg}$  was carried out in quartz tubes under radiation from a PRK-7 mercury lamp. The decomposition was studied both under vacuum and in air. The tubes were evacuated by freezing (and subsequently thawing) the contents of the tube three times while evacuating the air the same number of times. The evacuated tubes were sealed, while the tubes in which the reaction was carried out in the presence of air were closed by means of cork stoppers. The weight of diphenylmercury taken in the individual experiments was 10-15 g, and the molar ratio of the starting materials was maintained constant [ $(\text{C}_6\text{H}_5)_2\text{Hg} : \text{C}_6\text{H}_{12} = 1 : 30$ ]. Decomposition varied from 60 to 90% when the tubes were irradiated with u.v. light for 100-150 hours. The extent of the decomposition was determined from the amount of mercury precipitated.

TABLE 1. Photodecomposition of Diphenylmercury\* in Cyclohexane.  
 $(\text{C}_6\text{H}_5)_2\text{Hg} : \text{C}_6\text{H}_{12}$  (Mole) = 1 : 30

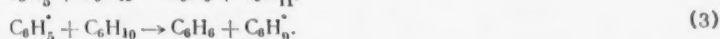
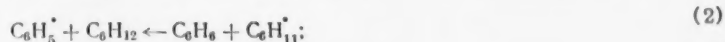
Reaction products	Mole % of reaction products with respect to Hg precipitated			
	Vacuum		In air	
	Expt. No. 1	Expt. No. 2	Expt. No. 3	Expt. No. 4
In cyclohexane. $(\text{C}_6\text{H}_5)_2\text{Hg} : \text{C}_6\text{H}_{12}$ (mole) = 1 : 30				
Benzene	150.3	159.9	162	163.6
Bicyclohexyl	46.9	45.8	27.9	38.0
Cyclohexene	30.1	32.9	32.8	22.16
Phenylcyclohexane	2.5	5.7	7.2	3.5
Biphenyl	4.1	3.8	11.5	6.3
In cyclohexene $(\text{C}_6\text{H}_5)_2\text{Hg} : \text{C}_6\text{H}_{10}$ (mole) = 1 : 30				
Benzene	157	152		
Bicyclohexenyl	70	74		

\* Both the number of moles of mercury precipitated and the number of moles of diphenylmercury decomposed were taken as 100%.



The experiments (Table 1) showed that the photodecomposition of diphenylmercury in cyclohexane yields mercury, benzene, bicyclohexyl, cyclohexene, and very small amounts of biphenyl and phenylcyclohexane. In addition, when the reaction was carried out in air, cyclohexanol and cyclohexanone were obtained. Mercury, benzene, and bicyclohexenyl were found when the  $(C_6H_5)_2Hg$  was decomposed in cyclohexene (Table 1).

It is apparent from the table that the phenyl radicals of the organomercury compound are predominantly converted to benzene (75-80%) during photodecomposition of diphenylmercury in cyclohexane and in cyclohexene. In contrast to the reaction in benzene, which takes place in the reaction complex [1], the reaction of diphenylmercury with cyclohexane and cyclohexene takes place by a free radical mechanism. Phenyl radicals formed by dissociation of the organomercury compound abstract hydrogen from the solvent, regenerating secondary radicals:



The latter can dimerize, disproportionate, and react with other radicals.

In the case of cyclohexene, there are two probable routes for the formation of benzene: from the benzene rings of the diphenylmercury and from extensive dehydrogenation of the solvent by phenylradicals. In order to clarify the situation, we carried out experiments on the photodecomposition and the thermal decomposition of diphenylmercury labeled with  $C^{14}$  in ordinary cyclohexene. It was found that the isotope composition of the benzene resulting from the reaction was identical to that of the original diphenylmercury. This indicates that dehydrogenation of cyclohexene with the removal of four hydrogen atoms does not take place. The benzene is formed only from the radicals of the organomercury compound. In our opinion, elimination of hydrogen from cyclohexene takes place predominantly at the  $\alpha$ -carbon atoms. The resulting bicyclohexenyl probably contains isolated double bonds. There are indications in the literature [2] that the reaction of peroxides with cyclohexene is accompanied by dehydrodimerization of the latter; here, capture of hydrogen from the solvent occurs predominately at the allyl position.

Moreover, it should be remarked that the decomposition of  $(C_6H_5)_2Hg$  in cyclohexene is significantly accelerated by peroxide compounds, which, as is well known [3], can readily be formed during storage of cyclohexene in air. Therefore, in our work we used cyclohexene which had been freshly distilled over sodium in an atmosphere of nitrogen.

As may be seen from Table 1, considerably less bicyclohexenyl and cyclohexene are obtained when the photodecomposition of diphenylmercury in cyclohexane is carried out in air than when the reaction is carried out under vacuum. It is probable that the cyclohexyl radicals are oxidized by the oxygen of the air to cyclohexanone and cyclohexanol, the presence of which in the reaction mixture was proved.

The thermal decomposition of diphenylmercury in cyclohexane was carried out in glass tubes at 260-280°. It was not possible to carry out the reaction with large volumes of the material at these temperatures. Therefore, not more than 2-3 g of the organomercury compound was used, and the mole ratio of the starting materials was kept the same as in the photodecomposition experiments. The extent of the reaction did not exceed 15-20% after 50 hours heating in the majority of the experiments. There was 8.7% reaction in 150 hours at 260°. Mercury, benzene, cyclohexene, phenylcyclohexane, and traces of biphenyl were obtained in this case. We were unable to detect bicyclohexenyl in the reaction mixture. In contrast to photodecomposition, thermal decomposition is accompanied by the formation of a considerable amount of a difficultly soluble polymeric compound  $(-C_6H_4-Hg-)_n$ ; we have previously observed the formation of this substance during reactions of diphenylmercury with other solvents.

Analysis of the reaction product was carried out with an IKS-14 infrared spectrophotometer; the frequency range covered was 400-2000  $cm^{-1}$ . Quantitative determination of the components was accomplished by means of a calibration graph showing optical density (D) as a function of concentration (C, %). The benzene and cyclohexene were quantitatively determined in the cyclohexane solution distilled after the reaction; the frequencies used were 1820 and 720  $cm^{-1}$ . The remaining reaction products were steam distilled and dissolved in carbon tetrachloride. The contents of bicyclohexyl, biphenyl, and phenylcyclohexane were determined from bands at 600, 545, and 525  $cm^{-1}$ , respectively. In the case of the reaction in cyclohexene, the benzene was quantitatively determined by the isotope dilution method. A weighed amount of benzene labeled with  $C^{14}$  was introduced into the reaction mixture. After the solution was stirred, the benzene was separated in the form of *m*-dinitrobenzene and analyzed for  $C^{14}$  content. The bicyclohexenyl was separated from the reaction mixture by steam distillation. It was redistilled under vacuum, and the molecular weight, elemental composition, and double bonds were determined.

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# SULFONATION OF 2-VERATRYL- AND 2-PIPERONYL- -1,3-INDANDIONES

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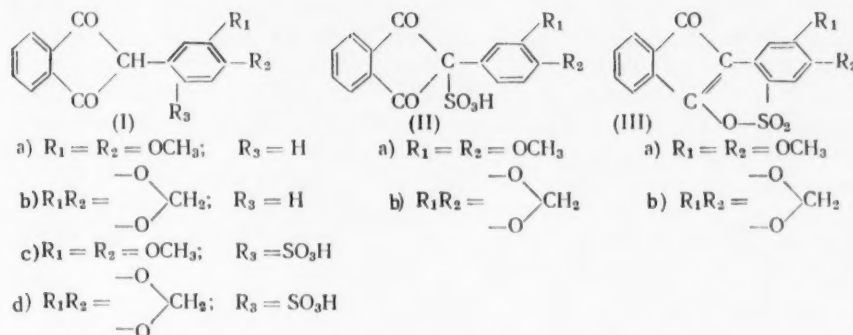
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In a continuation of our work [1,2] on the sulfonation of 2-monosubstituted 1,3-indandiones, we have carried out the sulfonation of 2-veratryl- and 2-piperonyl-1,3-indandiones (Ia and Ib), which led to the formation of bright red cyclic enol sulfonates—sultones (IIIa and IIIb)—together with the expected 2-veratryl- and 2-piperonyl-1,3-indandione-2-sulfonic acids (IIa and IIb).

The sulfonation was carried out by methods previously used for cyclic  $\beta$ -diketones [1,3,4]: with dioxane—sulfur trioxide ( $D \cdot SO_3$ ), concentrated sulfuric acid in the presence of acetic anhydride, and chlorosulfonic acid in 1,2-dichloroethane solution. Regardless of the sulfonating agent used, sulfonic acids (IIa and IIb) and enol sulfonates (IIIa and IIIb) were simultaneously formed.



In sulfonations with concentrated sulfuric acid in the presence of acetic anhydride there was a strong dependence of the ratio of the amounts of sulfonation products II and III on reaction time. When water was added to the reaction mixture after 3-5 minutes, the yield of IIa and IIb was 30-40%, while the yield of IIIa or IIIb was 25-30%; an increase in the reaction time led to an increase in the yield of sulfonates (III) to 70%, and the yield of II was insignificant. When the sulfonating agent was chlorosulfonic acid or  $D \cdot SO_3$ , enol sulfonates (III) invariably greatly predominated in the reaction products, and the yield of II did not exceed 5%.

The free acids (IIa and IIb) were not isolated; their sodium salts crystallized readily from dilute alcohol. The sulfonic acid group in the 2 position is not strongly bonded, and could be replaced by the action of bromine. The presence of the sulfonic acid group at the secondary carbon atom was confirmed by u.v. and i.r. absorption spectra.\* It is known [5] that the diketone form of  $\beta$ -diketones of the 1,3-indandione series are characterized by an intense absorption in the region of 220-240  $m\mu$ , and this band was observed for compounds IIa and IIb (Fig. 1).

In the i.r. spectra, carbonyl bands at 1703 and 1741  $cm^{-1}$  (IIa) and at 1705 and 1746  $cm^{-1}$  (IIb) also correspond to the diketone form. Acids IIa and IIb were characterized in the form of the benzylthiuronium salts.

\*The u.v. spectra were taken in methanol solution using an SF-4 apparatus. The i.r. spectra were taken with suspensions in paraffin oil or in solution in 1,2-dichloroethane using an IKS-12 apparatus.

It is known [1,2] that chlorosulfonic acid readily sulfonates the phenyl radical of 2-phenyl-1,3-indandiones in the para-position. In the case of 2-veratryl- and 2-piperonyl-1,3-indandiones sulfonation of the radical was facilitated by the presence of electron donor substituents, and sulfonation of the radical was accomplished even with the sulfuric acid-acetic anhydride mixture and with  $D\cdot SO_3$  in the sterically less hindered ortho-position. Furthermore, it is evident that interaction of the sulfonic acids with the enol form of the diketones takes place. The molecular weight of the resulting compounds (IIIa and IIIb) shows that such interaction is intramolecular. Of the three possible isomers formed by sulfonation of the veratryl or piperonyl ring, we felt that the most probable would be IIIc or IIId, the formation of which is sterically less hindered.

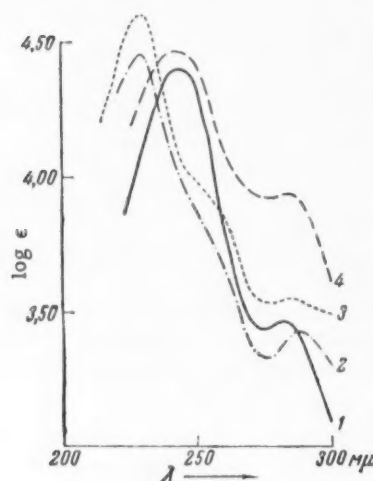


Fig. 1. Ultraviolet absorption spectra; in methanol: 1) IIIa, 2) IIb, 3) IIa, 4) IIIb.

Compounds IIIa and IIIb are insoluble in basic and alcoholic alcoholate solutions. The ester group is cleaved by alcoholic alkali with the formation of 2-monosubstituted 1,3-indandiones containing a sulfonic acid group in the veratryl (piperonyl) radical (Ic and Id). The presence of a free hydrogen atom at the secondary carbon was demonstrated chemically; compounds Ic and Id dissolved in a base with the formation of a red solution, and, in contrast to IIIa and IIIb, they were readily brominated. The Br in the bromination products was polarized positively, which is characteristic of 2-bromo-1,3-indandiones [1].

The structure of the intramolecular enol sulfonates (IIIa and IIIb) were also confirmed by their i.r. and u.v. absorption spectra. In the ultraviolet region, compounds IIIa and IIIb absorb at 240-250 mμ, which is characteristic [5] of the enol configuration of 1,3-indandiones (Fig. 1).

The infrared data are presented in Table 1. The correct interpretation of these data requires special comment. The presently available data on the characteristic frequencies of 1,3-indandione derivatives [5] shows that the dicarbonyl form is characterized by two absorption maxima, a very intense band at  $1700-1720\text{ cm}^{-1}$  and a weak absorption at  $1730-1760\text{ cm}^{-1}$ . The formation of derivatives of the enol forms only very slightly shifts the first carbonyl group frequency, while the second disappears. Consequently, it is impossible to estimate the diketone and enol structures with complete assurance from the shift in the carbonyl frequencies in indandione systems. However, it was found that these structures can easily be distinguished on the basis of the intensity of the absorption. The diketone form was characterized by an intensity of  $\epsilon = 800-1200$ . Moreover, the presence of an enol configuration could be determined on the basis of a low-intensity absorption in the  $1625-1635\text{ cm}^{-1}$  region, which is provisionally assigned to the double bond.

TABLE 1

Substance	State	Characteristic frequencies in the $1500-1800\text{ cm}^{-1}$ region*
2-Veratryl-1,3-indandione (Ia)	Solid	1519 (83), 1590 (69), 1701 (88), 1741 (50)
	In dichloroethane	1715 ( $\epsilon = 1200$ ), 1749 ( $\epsilon = 380$ )
1-Piperonyl-1,3-indandione (Ib)	Solid	1506 (61), 1578 (38), 1601 (38), 1702 (85)
	In dichloroethane	1744 (42)
Veratrylindandione sulfonate (IIIa)	Solid	1715 ( $\epsilon = 980$ ), 1751 ( $\epsilon = 250$ )
	In dichloroethane	1520 (100), 1604 (79), 1635 (60), 1713 (82)
Piperonylindandione sulfonate (IIIb)	Solid	1717 ( $\epsilon = 580$ )
	In dichloroethane	1512 (66), 1584 (55), 1628 (55), 1628 (55), 1720 (75)
Methyl ester of 2-phenyl-1,3-indandione	Solid	1719 ( $\epsilon = \sim 400$ )
	In dichloroethane	1580 (80), 1630 (70), 1690 (75)
	In dichloroethane	1711 ( $\epsilon = 400$ )

\* Only the carbonyl group region was scanned for the dichloroethane solutions.

The simple route for the synthesis of unusual condensed polycyclic sultones (IIIa and IIIb) and the spectroscopic

method of distinguishing diketone and enol structures in the 1,3-indandione series can be of considerable interest in the field of  $\beta$ -dicarbonyl compounds.

#### EXPERIMENTAL

Sulfonation of 2-veratryl- and 2-piperonyl-1,3-indandiones with a mixture of sulfuric acid and acetic anhydride. A mixture of 1.1 ml of sulfuric acid and 6 ml of acetic anhydride in 10 ml of 1,2-dichloroethane was added to 2.83 g of Ia (2.66 g of Ib) in 25 ml of 1,2-dichloroethane. A crystalline orange precipitate began to separate from the dark red transparent mixture after 5-10 minutes. After 1 hour, the solidified mass was treated with 50 ml of water, the insoluble material was separated by filtration, and the aqueous layer was separated from the 1,2-dichloroethane layer. The water layer was neutralized with sodium bicarbonate and saturated with sodium chloride. The amount of the sodium salt of IIa salted out of solution was 0.2 g (about 5%); correspondingly, the amount of IIb was 0.5 g. The substance was crystallized from dilute alcohol and dried at 110°. The resulting crystals were white. The material was soluble in water and insoluble in organic solvents; it dissolved in bases forming colorless solutions. IIa Found %: S 8.09.  $C_{17}H_{13}O_7SNa$ . Calculated %: S 8.34. IIb Found %: S 8.45.  $C_{16}H_9O_7SNa$ . Calculated %: S 8.71.

The benzylthiuronium salts of IIa and IIb were prepared by mixing aqueous solutions of the sodium salts of IIa and IIb with an aqueous solution of benzylthiuronium chloride. The benzylthiuronium salt of IIa was obtained in the form of white prisms (from alcohol). M.p., 201°. Found %: N 5.42; S 12.01.  $C_{25}H_{24}O_7N_2S_2$ . Calculated %: N 5.30; S 12.13. The benzylthiuronium salt of IIb was also in the form of white prisms (from alcohol). M.p., 200°. Found %: N 5.46; S 12.33.  $C_{24}H_{20}O_7N_2S_2$ . Calculated %: N 5.47; S 12.51.

The orange precipitate of IIIa (IIIb) was crystallized from 200 ml of acetic acid. There was obtained 2.1 g of IIIa (correspondingly, 2 g of IIIb). The IIIa was in the form of matted orange crystals. It was difficultly soluble in chloroform and benzene and insoluble in alcohol, acetone, water, and bases. M.p., 251°. Mol. wt. (Rast), 320-330. Calculated %: 344.3. Found %: S 9.06.  $C_{17}H_{12}O_6S$ . Calculated %: S 9.31. The IIIb was in the form of bright red crystals. The solubility was the same as for IIIa. M.p., 257°. Found %: S 9.45; 9.49.  $C_{16}H_8O_6S$ . Calculated %: S 9.77.

Sulfonation of Ia and Ib with chlorosulfonic acid or  $D \cdot SO_3$  was carried out similarly to the sulfonation with sulfuric acid. From 2 to 3 moles of the sulfonating agent was taken for each mole of the dione (Ia or Ib). The yield of IIa (IIb) was insignificant; the yield of IIIa (IIIb) was 60-70%.

Cleavage of IIIa with alcoholic alkali. A mixture of 3.44 g of IIIa, 80 ml of alcohol, and 4 g of finely powdered sodium hydroxide was refluxed for 1 hour on a water bath. A transparent red solution was formed. The alcohol was distilled. The residue was dissolved in 40 ml of water, and the solution was made acid with hydrochloric acid and saturated with sodium chloride. A yellow precipitate of the sodium salt Ic was salted out. It was crystallized from 96% alcohol. Found %: S 8.52.  $C_{17}H_{13}O_7SNa$ . Calculated %: S 8.71.

Bromination of Ic was carried out in an aqueous bromine solution. The bromination product was salted out with sodium chloride and crystallized from dilute alcohol. The bromine derivative liberated iodine from an acid solution of potassium iodide. Found %: Br 17.03; S 7.05.  $C_{17}H_{12}O_7BrSNa$ . Calculated %: Br 17.25; S 6.92.

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# THE EFFECT OF HYDROGEN AND OF ARGON ON ELECTROCRACKING OF METHANE AND ETHYLENE

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(Presented by Academician B. A. Kazanskii, June 7, 1961)

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The effect of hydrogen on the electrocracking of methane has repeatedly been discussed in the literature. Some authors have claimed that hydrogen inhibits carbon deposition [1]. S. S. Vasil'ev proposed that hydrogen activates cracking under certain conditions and inhibits it under others [2]. According to D. Koller [3], the over-all conversion of methane is increased by the presence of hydrogen. Now this question is important both with respect to practical applications and for an understanding of the mechanism of electrocracking; therefore, we have carried out an investigation in which the effect of hydrogen on the process was compared with the effect of chemically inert argon. The effect of hydrogen and of argon on the electrocracking of ethylene and other hydrocarbons was also studied.

## EXPERIMENTAL

The work was carried out under static conditions, using an apparatus described earlier [5]. The degree of conversion ( $\Delta$ ) was determined by measuring the pressure, it being assumed that decomposition of the hydrocarbon took place mainly by two routes:



which are characterized by identical volume changes. The manner in which an experiment was carried out is as follows. Hydrogen or argon was added to the hydrocarbon at a predetermined partial pressure until the total pressure acquired the desired value of 50 or 150 mm Hg. The discharge was then switched on at various intermediate times ( $\tau$ ). After an alternate switching on and quenching of the discharge, the pressure was measured. The current was 300 ma in all experiments. The gas was analyzed at the end of the experiment, when the conversion had reached approximately 50%.

Figure 1 presents the time dependence of the average rates of methane and ethylene decomposition and also of mixtures of these hydrocarbons with hydrogen and with argon. The decomposition rate of methane and of ethylene were of the same order when the hydrocarbon partial pressure was 40 mm Hg. As may be seen from the figure, the addition of argon or hydrogen inhibited cracking of both hydrocarbons to approximately the same extent, and inhibition was greater the higher the partial pressure of the added gas. Thus, at a total pressure of 150 mm Hg, the rate of decomposition of the hydrocarbons drops to approximately half. With a decrease in initial hydrocarbon pressure to 10 mm Hg and in the absence of added gas, methane cracked significantly more slowly than ethylene (by a factor of 50). In this case, dilution of the ethylene with hydrogen or argon produced the cracking inhibition noted above. When the same gases were added to methane, the process was sharply activated, and the rate of methane cracking approached the rate of ethylene decomposition under the same conditions. It is characteristic that the external appearance of the discharge changed during activation of the cracking process. At  $P=40$  mm Hg, the discharge in an atmosphere of pure hydrocarbon or in argon- or hydrogen-containing mixtures was yellow and slightly smoky, while at  $P=10$  mm Hg the discharge in methane had a bluish luminescence which changed to an intense yellow with the addition of hydrogen or argon. In the case of ethylene at this pressure, the discharge was yellow.

Thus, activation of methane cracking is observed with an increase in the total methane pressure and also with the addition of hydrogen and, to a still greater extent, of argon. Activation of the process also occurred during the course of a single experiment under the following conditions: initial methane pressure of 50 mm Hg, current of 50 ma, and a distance between electrodes of 28 mm. The initial discharge was light yellow at the electrodes, which

were covered with a glowing luminescence. However, at some time after the start of the experiment the discharge became localized between incandescent points on carbonaceous growths formed on the electrodes. At the same time, the weak luminescence changed to an intense yellow, and the cracking rate increased by a factor of ten. When the experiment was begun with electrodes initially covered with these carbonaceous growths or with other tarry substances, the cracking rate was immediately significant, and the discharge was a smoky yellow. It is characteristic that acceleration during the course of the cracking did not occur either at high or at low pressures. In the first case, the discharge was activated regardless of the state of the electrode surfaces; in the second case, the very slight increase in current density as a consequence of partial localization of the discharge was apparently insufficient for the discharge to become active.

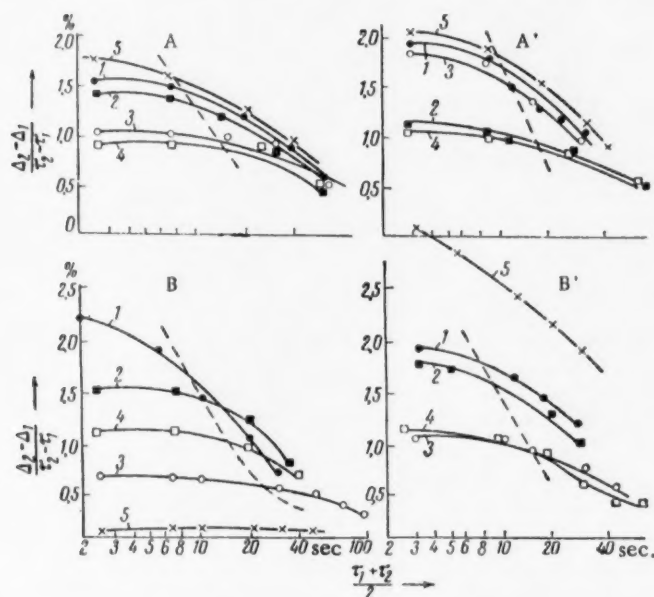


Fig. 1. Change in rate of total conversion of methane (A, B) and ethylene (A', B') with time in the presence of hydrogen and argon.  $\Delta$ —degree of hydrocarbon conversion corresponding to a discharge time  $\tau$ .

Fig.	Curve no.	Partial pressure (in mm)			Fig.	Curve no.	Partial pressure (in mm)		
		hydro-carbon	hydro-gen	argon			hydro-carbon	hydro-gen	argon
A, A'	1	40	0	[10]	B, B'	1	10	0	40
	2	40	0	[110]		2	10	0	140
	3	40	10	[/]		3	10	40	0
	4	40	110	[/]		4	10	140	0
	5	40	0	0		5	10	0	0

Points of intersection of the kinetic curves with the broken line corresponding to a hydrocarbon conversion of 15-18%.

Thus, activation of electrocracking of methane can apparently be due to different causes (an increase in pressure, an increase in current, localization of the discharge between hot spots), and is apparently dependent on a transition of the discharge from a slightly active glow discharge to a chemically more active arc discharge. The latter is characterized by higher values of the molecular temperature, the positive role of which during electrocracking of hy-

drocarbons has previously been noted [3,6]. Speaking of general considerations of the mechanism of the chemical action of the discharge, we may propose that only processes having a significant activation energy (rupture of C-C and C-H bonds) undergo electronic activation. Further chain development of the process takes place with the participation of the resulting atoms and radicals, and it requires thermal activation, i.e., comparatively high temperatures. The idea of a chain mechanism for the process is confirmed by the high values of the thermal coefficient (0.4-0.6) obtained for hydrocarbon cracking [5].

In our opinion, all of the above conclusively proves the absence of a specific effect of hydrogen on the intensity of electrocracking of hydrocarbons.

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# THE MECHANISM OF REARRANGEMENT OF IMIDOETHERS

A. E. Arbuzov and V. E. Shishkin

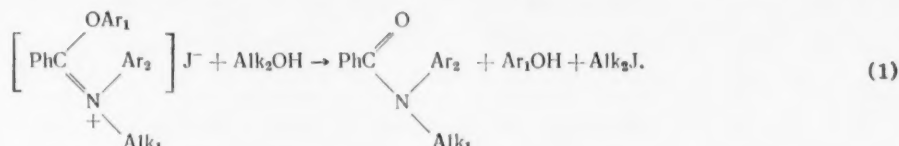
Kazan S. M. Kirov Institute of Chemical Technology

Translated from Doklady Akademii Nauk SSSR, Vol. 141, No. 3,

pp. 611-612, November, 1961

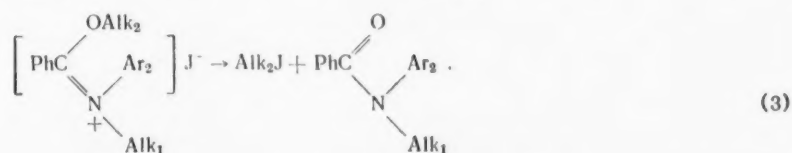
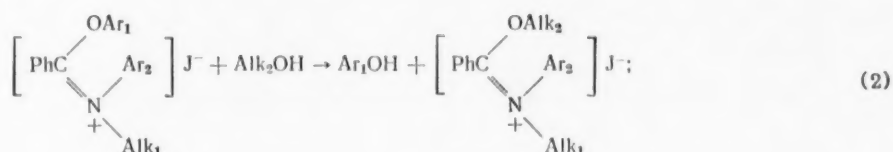
Original article submitted August 3, 1961

Wheeler [1] and Lander [2] suggested that rearrangement of imidoethers to substituted amides on reaction with alkyl halides proceeds through the stage of formation of an intermediate addition product. No experimental proof of this hypothesis has hitherto been obtained. The alkyl iodides of aryl benzimidooethers that we prepared [5] are the only known products of addition of alkyl halides to imidoethers. Decomposition of the alkyl iodides on heating does not, however, give the N-alkylbenzanilides—products of rearrangement of imidoethers. Success followed a study of the reaction of the alkyl iodides of the imidoethers with alcohols. It was found that reaction with boiling alcohol leads to formation of N-alkylbenzanilide, phenol, and alkyl iodide according to the equation:



The conversion of imidoether to amide was thus realized, so that alkyl iodides are intermediates in the rearrangement of imidoethers.

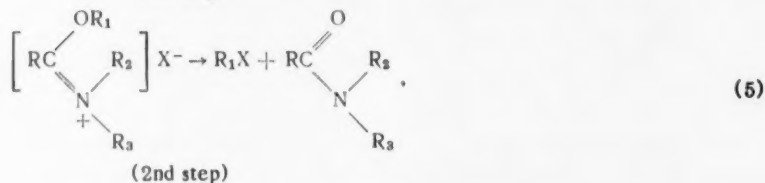
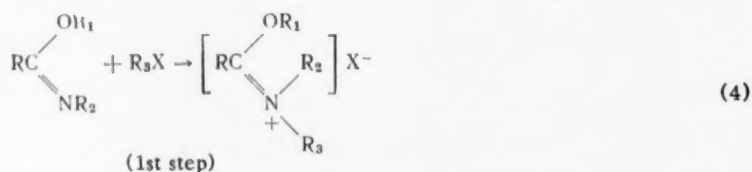
We consider that the first step of reaction (1) is transesterification with formation of phenol and an unstable alkyl halide of the alkyl imidoether (2) which quickly and spontaneously undergoes conversion to the amide with separation of alkyl iodide (3):



The occurrence of reaction (2) is confirmed by study of the products of reaction of N-phenylbenzimidophenyl ether methiodide with ethyl mercaptan. The reaction does not take place in the boiling mercaptan, but at 100° a complex reaction takes place with resinification, and the reaction mass contains neither products of transesterification—phenol or thiophenol—nor the product of rearrangement of the imidoether (amide).

On the basis of the above evidence it is evidently permissible to assume that rearrangement (and isomerization as a special case) of alkyl imidoethers under the influence of alkyl halides proceeds in two steps with formation of an unstable intermediate addition product whose structure, like that of alkyl iodides of aryl imidoethers, is probably of an ionic type. Rearrangement is completed by migration of the oxygen of the ether group of radical R in the form of a cation to the anion of the halide X.

In a generalized form the mechanism of rearrangement may be represented by the following scheme:



Various mechanisms of the second step are evidently possible, and this step requires further investigation.

#### EXPERIMENTAL

Reaction of N-phenylbenzimidophenyl ether methiodide with ethyl alcohol. A mixture of 25 g of methiodide and 40 ml of absolute alcohol was gently boiled for 1.5 hr. A colorless 72-80° fraction was distilled from the homogeneous reaction mass at normal pressure. Dilution of this fraction with water gave a heavy liquid with b.p. 72-73° and  $n_D^{20}$  1.5171 which was identified as ethyl iodide.

Yield of ethyl iodide 6.8 g (73% of theory). Distillation of the residual reaction mass in vacuo gave fractions with b.p. 75-78° (10 mm) and 147-149° (1.5 mm). The 75-78° (10 mm) fraction distilled at normal pressure at 179-182° and crystallized completely. M.p. 41-42°. Judging by its properties, the substance was phenol. Yield of phenol 5.1 g (89.5% of theory). The 147-149° (1.5 mm) fraction crystallized completely after seeding with methylbenzanilide. Recrystallization gave 9.5 g of methylbenzanilide with m.p. 60-61° (yield 75% of theory). Found %: C 79.68; 79.62; H 6.00; 6.18; N 6.78; 6.86.  $\text{C}_{14}\text{H}_{13}\text{NO}$ . Calculated %: C 79.59; H 6.20; N 6.62.

Literature data [3,4]: m.p. 59°; b.p. 195°, 12 mm.

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# THE MECHANISM OF POLYMERIZATION OF EPICHLOROHYDRIN OVER THE CATALYTIC SYSTEM $\text{FeCl}_3$ -PROPYLENE OXIDE

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In a study of the process of polymerization of epichlorohydrin on the catalytic system  $\text{FeCl}_3$ -propylene oxide we showed [8] that the monomer/catalyst molar ratio regulates not only the average molecular weight but probably also the fine details of the kinetics of polymerization. It is suggested that with low catalyst concentrations the process takes place in two steps: initially at primary catalytic centers there occurs relatively rapid growth of chains accompanied by gradual inactivation of the primary centers. Polymerization commences at the catalyst formed from anhydrous ferric chloride and propylene oxide. However, the concurrent detachment of a kinetic chain from the primary active centers leads to formation of a new catalytic complex [ $\text{FeCl}_3$ -epichlorohydrin] which is also capable of initiating polymerization but at an appreciably different rate [1]. So long as first order centers are present, they substantially completely suppress this secondary process. But with increasing degree of conversion (which increases approximately in inverse ratio to the concentration of primary active centers at a given instant) the secondary centers begin to play a more important part which ultimately predominates. With large initial concentrations of catalyst, the primary centers cannot be fully consumed during the process and we can therefore expect polymerization to proceed only at the primary active centers ( $\text{FeCl}_3$ -propylene oxide).

An attempt was made to check this hypothesis by investigating samples of polyepichlorohydrin obtained under otherwise identical conditions with catalyst concentrations equal to 2, 5, and 10 wt.-% of monomer. If two systems of active centers were simultaneously present, or acted in succession, in the polymerizing system, then we should expect the corresponding molecular weight distribution to be bimodal [2].

The distribution in terms of sedimentation coefficients is plotted in Fig. 1. These coefficients were found by ultracentrifuging under identical conditions ( $C = 0.5\%$ ,  $T = 25^\circ$ ,  $n = 60,000$  rpm) without allowance for concentration effects and diffusion. These conditions are fully adequate for comparison purposes since the shape of the sedimentation curves give sufficient information for confirmation or refutation of the basic hypothesis.

## EXPERIMENTAL

Preparation of monomer. The commercial product was dried for five days over anhydrous calcium chloride and then fractionated in a 30-plate column. The 114-115° (760 mm mercury column) fraction was investigated. The epichlorohydrin had the following constants:  $n_D^{20}$  1.4370,  $d_4^{20}$  1.1806,  $M_R$  found 20.54, calculated 20.61. Literature [3]:  $n_D^{20}$  1.4364,  $d_4^{20}$  1.1801.

Preparation of catalyst. Components were sublimed ferric chloride and propylene oxide, and the literature method was employed [4]. The dark-brown, viscous paste contained Fe 15.06%, C 37.33%, H 6.49%. It was dissolved in anhydrous, chemically pure acetone. Catalyst concentration 0.6 g/ml.

Polymerization procedure. A solution of catalyst of known concentration was placed in a glass ampoule which had previously been dried in vacuo and filled with nitrogen. The acetone was removed in vacuo at room temperature. Monomer was then introduced into the ampoule which was again filled with nitrogen and sealed off. The ampoules were placed in a casing which was thermostatted at 80° for 24 hr.

Treatment of polymer. The crude polymer was dissolved in hot acetone, and the solution acidified with HCl (for removal of iron as  $\text{FeCl}_3$ ). After cooling, the acetone solution, containing the precipitated high-molecular fraction, was diluted with a large volume of water. Low-molecular fractions were thereby brought which were soluble

in cold acetone. The polymer was filtered off and dried to constant weight in vacuo at 50°. Solutions for sedimentation measurements were prepared by dissolving 0.5% of polyepichlorohydrin in tetrahydrofuran.

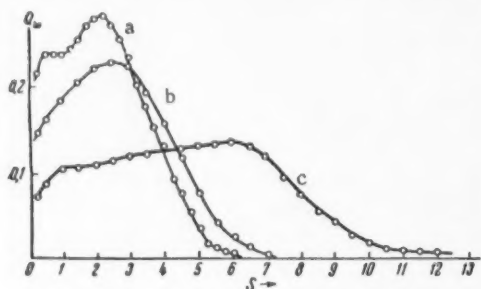


Fig. 1. Distribution of sedimentation constants of epichlorohydrin: a) No. 1936 (5% catalyst)  $[\eta] = 0.976$ ; b) no. 1938 (10% catalyst)  $[\eta] = 0.985$ ; c) no. 1937 (2% catalyst)  $[\eta] = 1.33$ .

**Sedimentation.** Experiments for determination of the distribution function on the basis of sedimentation constants were carried out in a large Svedberg oil centrifuge at a speed of  $6 \times 10^4$  rpm. The sedimentation was observed with the help of a Philpot-Svensson optical system with a phase-contrast diaphragm. Experiments were carried out at a temperature of  $25 \pm 0.5^\circ$ . The resulting sedimentation photodiagrams were processed by the usual technique [5].

The characteristic viscosity was determined at 25° in an Ostwald viscometer with a suspended level. The period of discharge of the solvent (tetrahydrofuran) was of the order of 100 sec. Extrapolation to zero velocity gradient of discharge was not carried out due to the relatively low (approximately  $10^6$ ) molecular weights of the investigated samples [6].

The partial specific volume of polyepichlorohydrin in tetrahydrofuran was found pycnometrically at  $T = 25^\circ$ .

#### EVALUATION OF RESULTS

We see from Fig. 1 that the highest molecular and most disperse polymer is obtained with a catalyst content of 2%. The residue of low-molecular maximum in the region  $S=1$  is easily visible. A certain distortion of the distribution curve is caused by the superposition of the primary and secondary distributions. The total fall in molecular weight (shift of the curve as a whole towards smaller values of  $S$ ) is consistent with the results of characteristic viscosity measurements (Fig. 2). With 10% catalyst concentration the secondary maximum disappears and the distribution becomes unimodal. We can therefore conclude that in the latter case there is only one (primary) mechanism of chain growth.

The average molecular weight  $M_{S\eta}$  can be roughly evaluated from the Flory-Mandelkern formula [7]:

$$2.5 \cdot 10^6 = \frac{\eta_0 N_A}{1 - v\rho} S ([\eta] / M^2)^{1/2},$$

where  $\eta_0$  = viscosity of the solvent;  $N_A$  = the Avogadro number;  $v$  = partial specific volume;  $\rho$  = density of solution;  $S$  = sedimentation constant;  $[\eta]$  = characteristic viscosity;  $M$  = molecular weight ( $M_{S\eta}$ ). The value obtained for the sample with 2% catalyst is  $1 \times 10^5$ . For each of the other two samples (5 and 10% catalyst) the average value is  $2.5 \times 10^4$ .

The hypothesis of a two-stage mechanism of this polymerization on primary and secondary catalytic centers is thereby confirmed on the basis of statistical analysis of sedimentation diagrams, obtained under identical conditions, of three samples of polyepichlorohydrin synthesized on the catalytic system  $[\text{FeCl}_3 - \text{propylene oxide}]$  with various catalyst concentrations.

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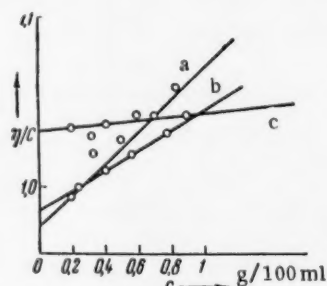


Fig. 2. Converted viscosity as a function of concentration. Details as in Fig. 1 (origin of the axis of the ordinates at 0.9).

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# CATALYTIC DEHYDROGENATION OF ALKYLPHENOLS

A. A. Balandin, G. M. Marukyan, and R. G. Seimovich

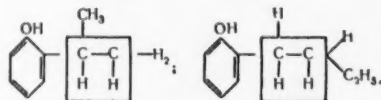
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The preparation of alkylphenols and of their derivatives with an unsaturated side chain was described 20-25 years ago [1-3]. At the same time their applications in various industries, in particular for the manufacture of resins, was also described. Phenols containing unsaturated side chains are mainly obtained by synthesis [4]. The literature contains no data for the catalytic dehydrogenation of alkylphenols; it was therefore of interest to extend our work on dehydrogenation [5,6] to these compounds. In the present investigation we established that butyl- and isopropylphenols are dehydrogenated with facility while retaining the phenolic hydroxyl group. In terms of the multiplet theory, dublet reactions take place according to the following scheme (the reacting atoms in contact with the catalyst surface are enclosed in squares):



The results obtained are of definite interest and may be applied to the synthetic rubber, plastics, electrotechnical, paint, and other industries.

On comparing the results of dehydrogenation of butylphenol and isopropylphenol under approximately identical conditions (see tables), we see that butylphenol is more easily dehydrogenated than isopropylphenol. We can therefore conclude that the reactivity of the initial alkylphenols depends on their structure. We previously established [6] the law that the rate of dehydrogenation and the yield increase with increasing length of side chain in the alkylbenzene. This law also applies to alkylphenols.

## EXPERIMENTAL

**Starting substances.** Butylphenol and isopropylphenol were synthesized by the method of Tsukervanik and Nazarova [2]. Butylphenol: b.p. 108-110° (6 mm),  $n_D^{20}$  1.5181,  $d_4^{20}$  0.9717, in agreement with the literature data for o-butylphenol [2]. Isopropylphenol: b.p. 213-215°,  $n_D^{20}$  1.5173,  $d_4^{20}$  0.9730, which are close to the literature data [2] for o-isopropylphenol.

**Determination of unsaturated compounds in the catalyzate.** The amount of unsaturates in the catalyzate was determined by the bromometric method. Determination of unsaturates by the bromine method presented certain difficulties since phenol itself and its alkyl derivatives are brominated fairly easily. Bromination of phenols and their derivatives has been extensively studied [7], but the reaction has not yet been fully clarified. Attention has been drawn [8] to the need for taking into account such factors as concentration of acid, duration of bromination, bromination temperature, and excess of bromine. At the start we therefore decided to work out a procedure for analysis of the phenols which would be suitable for investigation of our mixtures. The procedure was essentially based on Rosenmund's method [9]. We first checked this method on the initial alkylphenols. We carried out bromination at room temperature with 0.1 N bromine solution for 5 hr. The bromine solution was always taken in excess. The percentage of unsaturates in the catalyzate was calculated by the formula:

$$x = \frac{(a \cdot F_1 - b F_2) M}{P \cdot 100 (2 + 4)},$$

where x = molar percentage of unsaturated compound in the mixture (in the present instance o-n-butenyl-2-phenol); M = molecular weight of the unsaturated compound obtained in the reaction; P = weight of sample of investigated sub-

stance;  $\underline{a}$  and  $\underline{b}$  = number of milliliters of solutions of bromine and thiosulfate;  $F_1$  and  $F_2$  = the factors of the latter; 2 = number of atoms of bromine adding on at the double bond (in the side chain); 4 = number of bromine atoms taken up by the ring.

Example: For bromination of butylphenol  $\underline{a}$  = 47.4 ml bromine solution, with factor  $F_1$  = 0.9494, was taken. Back titration consumed  $\underline{b}$  = 6.7 ml of thiosulfate with factor  $F_2$  = 1.01; weight  $P$  = 0.152 g. On substituting in the equation we find  $\underline{x}$  = 62%.

TABLE 1. Dehydrogenation of Butylphenol

Expt. no.	Initial substance	Experimental temp.	Rate of addition hr <sup>-1</sup>	Diluent	Duration of expt. min.	Yield of catalyzate, wt.-%	Conc. of unsaturates in catalyzate, wt.-%
Dehydrogenation of butylphenol							
1	Ethylbenzene	600	0.43	CO <sub>2</sub>	60	—	52.6
2	Butylphenol	495	0.44	—	30	86.4	63.5
3	"	500	0.44	—	195	89.5	67.4
4	"	510	0.43	—	—	93.9	65.8
5	Ethylbenzene	600	0.35	CO <sub>2</sub>	60	90.5	57.5
6	"	600	0.38	CO <sub>2</sub>	60	—	32.6
7	Butylphenol	500	0.32	—	60	94.9	57.6
8	Ethylbenzene	600	0.40	CO <sub>2</sub>	45	87.8	37.7
9	Butylphenol	500	0.43	CO <sub>2</sub>	60	84.4	64.9
10	Sec. butylbenzene	530	0.50	—	30	76.3	42.4
11	Butylphenol	530	0.50	—	180	78.0	45.0
12	"	550	0.50	—	90	77.6	46.5
13	Ethylbenzene	600	0.58	CO <sub>2</sub>	60	—	40.5
14	Butylphenol	505	0.48	—	45	91.9	43.8
15	"	535	0.40	—	30	89.5	53.9
16	"	535	0.40	CO <sub>2</sub>	50	89.0	48.9
17	"	530	0.43	—	45	93.3	50.5
18	Ethylbenzene	600	0.64	CO <sub>2</sub>	30	—	47.2
Dehydrogenation of isopropylphenol							
19	Ethylbenzene	600	0.44	CO <sub>2</sub>	—	95.4	38.2
20	Isopropylphenol	500	0.40	no CO <sub>2</sub>	—	90.9	48.1
21	"	500	0.44	CO <sub>2</sub>	—	95.0	51.7
22	Ethylbenzene	600	0.37	CO <sub>2</sub>	—	—	44.3
23	Isopropylphenol	550	0.39	no CO <sub>2</sub>	—	—	36.1
24	"	500	0.40	no CO <sub>2</sub>	—	—	35.5
25	"	525	0.60	no CO <sub>2</sub>	—	—	36.3
26	Ethylbenzene	600	0.44	CO <sub>2</sub>	—	—	46.3

Copper-chromium catalyst No. 4 was used for dehydrogenation of the alkylphenols. Experiments were run by the flow technique in presence of CO<sub>2</sub> as diluent and also without dilution at atmospheric pressure. Apparatus and procedure were the same as those described in our preceding publications [10, 11]. The tube was of quartz, and a thermocouple was inserted in the catalyst bed.

The activity of the catalyst was determined by passing alkylbenzenes at 600° before and after the experiments with alkylphenol. Results of the experiments (see Table 1) show that the catalyst is not poisoned and does not lose activity after alkylphenols have been passed over them.

Dehydrogenation of butylphenol. Results of experiments on dehydrogenation of butylphenol are set forth in Table 1. It is seen that butylphenol is easily dehydrogenated over copper-chromium catalyst at lower temperatures than are applicable for alkylbenzenes [5, 6] even in the absence of diluent. The percentage of unsaturates in the condensate is fairly high. Analysis of the exit gases (see Table 2) shows that side-chain detachment also occurs in addition to dehydrogenation of butylphenol; the exit gases contained, apart from hydrogen, methane, ethane, and ethylene.



The butenylphenol isolated from the condensate had b.p. 110-112° (5 mm),  $n_D^{20}$  1.5384,  $d_4^{20}$  0.9975. The product (*o*-butenyl-2-phenol) is readily soluble in alcohol and caustic alkali. From the *o*-butenyl-2-phenol was prepared 2-methylchroman  $C_8H_8$  by the method of Claisen and Tietze [12]. This product boiled at 220° as compared with 219.5-221° reported in the literature [12]. This confirmed that the product of the dehydrogenation reaction is *o*-butenyl-2-phenol; under the influence of HBr the double bond in the side chain can migrate from the  $\alpha$ - to the  $\beta$ -position.

TABLE 2. Analysis of the Gases

Expt. no.	Experimental temp., °C	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	O <sub>2</sub>	CO
14	505	0,0	6,4	33,6	39,6	19,7	0,0	0,0
15	535	0,0	9,2	24,1	42,2	21,9	0,6	0,0
16 *	535	0,0	18,7	8,2	33,6	23,1	0,0	16,8
2	495	0,0	2,8	80,7	12,1	4,6	0,1	0,0
4	500	0,0	7,4	45,5	37,5	9,4	0,0	0,0

\* Expt. 16 was performed with CO<sub>2</sub> dilution, so that the gas contains much CO<sub>2</sub>.

TABLE 3

Initial substance	Experimental temp., °C	Yield of catalyzate wt. -%	$n_D^{20}$	Concentration of unsaturates in catalyst, wt. -%
Copper-chromium catalyst				
Ethylbenzene	605	77.0	1.5235	55.0
Isopropylphenol	500	75.0	1.5295	43.4
"	"	73.5	—	46.9
Ethylbenzene	605	76.6	1.5165	42.0
Catalyst No. 40				
Ethylbenzene*	600	97.2	1.5195	47.0
Isopropylphenol	498	72.5	1.5240	45.5
<i>o</i> -Butylphenol	495	74.7	1.5250	58.5

\* Experiment with ethylbenzene carried out in presence of water (1:2).

Dehydrogenation of isopropylphenol. Experiments were carried out in presence of copper-chromium catalyst which had previously been reduced with hydrogen at 500°. Catalyst volume 20 ml. Diluent CO<sub>2</sub>. Flow rate 0.30 hr<sup>-1</sup>. Results are set forth in Table 3.

Results of experiments over another, less active, copper-chromium catalyst are set forth in Table 1. Yields of isopropenylphenol at 500° are fairly high.

Another oxide catalyst (No. 40 [13]) was tested for dehydrogenation of alkylphenols, and this gave high yields of unsaturates in the catalyzate. Results are set forth in Table 3.

The exit gases from dehydrogenation of isopropylphenol and butylphenol had the following compositions:

H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>
79.2	11.85	5.3	—	3.64
68.8	16.3	6.0	4.3	4.3

The analysis indicates that, also in the case of oxide catalyst No. 40, dehydrogenation is accompanied by removal of the side chain.

We can therefore conclude that butyl- and isopropylphenols are dehydrogenated over copper-chromium catalyst and over oxide catalyst No. 40 at atmospheric pressure without a diluent and with a diluent at 495-510° to give satisfactory yields of o-n-butenyl-2-phenol and isopropenylphenol. The catalyst is not poisoned and does not lose activity.

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# INVESTIGATION OF THE STRUCTURE OF UNSATURATED NITRO COMPOUNDS BY THE METHOD OF DIPOLE MOMENTS

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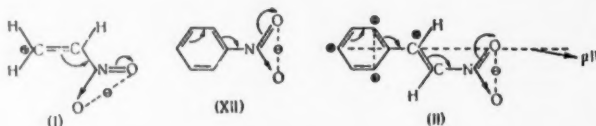
By means of the method of dipole moments it has become possible for the first time to establish the configuration of unsaturated nitro compounds and thereby to considerably extend our knowledge of the distribution of electron densities in these compounds.\*

The investigated substances (I-XI, see Table 1) could be assigned either a planar (cis or trans relative to the C=C bond) or non-planar configuration. Displacement of the nitro group from the plane of the benzene ring is energetically unfavorable due to the loss of  $\pi$ -conjugation in  $\beta$ -nitrostyrenes; moreover the loss of coplanarity ought to cause the dipole moments to approximate those of aliphatic nitro compounds, but this is not the case. The hypothesis of a non-planar structure of the investigated substances is therefore invalid.

The cis-structure is excluded in planar configurations due to the discrepancy between the values of the measured moments ( $\mu$ ) and those of the vector sums of the moments of individual bonds ( $\mu \Sigma_1$  cis) calculated for cis-forms. Another factor that makes planar cis-configurations unlikely is the considerable degree of steric hindrance resulting from the small distance between the hydrogen atoms of the benzene ring and the oxygen of the nitro group (the distance between the centers of these atoms in  $\beta$ -nitrostyrenes is  $\sim 0.3$  Å, Fig. 1; in furylnitroethylene it is  $\sim 0.5$  Å).

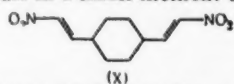
The similarity in the values of the experimental moments and those calculated on the assumption of trans-configuration ( $\mu \Sigma_1$  trans) and the absence of steric hindrance permitted the assignment of trans-structure to  $\beta$ -nitrostyrenes; for example, for substance V  $\mu = 7.68$ ,  $\mu \Sigma_1$  trans = 6.120,  $\mu \Sigma_1$  cis = 3.84; for substance VI  $\mu = 1.00$ ,  $\mu \Sigma_1$  trans = 0.50,  $\mu \Sigma_1$  cis = 7.38.

Conjugation of the nitro group with the double bond and the benzene ring leads to development of a supplementary conjugative moment which ought to increase with increasing number of conjugated  $\pi$ -bonds and with increasing distance between  $\delta^-$  and  $\delta^+$ ; in vectorial association with the moment of the  $\text{NO}_2$  group itself  $\mu_{\text{C}_2\text{H}_5\text{NO}_2} = 3.2$  D) it should lead to increase in the over-all moment in the sequence  $\mu_{\text{C}_2\text{H}_5\text{NO}_2} (3.2 \text{ D}) < \mu_{\text{I}} (3.41 \text{ D}) < \mu_{\text{XII}} (4.01 \text{ D}) < \mu_{\text{II}} (4.51 \text{ D})$ . This is actually the case.



For the same reason, and also because the stronger electronic gap at the  $\alpha$ -carbon atom makes the polarity of the  $\text{C}_\alpha$ -H bond greater than that of the  $\text{C}_\beta$ -H bond, the vector of the moment of the  $\beta$ -nitrovinyl group should deviate from the direction of the phenyl- $\text{C}_\alpha$  bond, i.e., this group should be "irregular."

The moments of substances X and XI provide good confirmation of this conclusion. In 1,4-bis-( $\beta$ -nitrovinyl) benzene (X), the two nitrovinyl groups can be either trans or cis in relation to the benzene ring.\*\* The dipole moment of the trans-form should be equal to zero due to the complete condensation of the vectors of the moments of the  $\text{NO}_2$  groups. Cis-configuration should result in a small moment owing to irregularity of the  $\beta$ -nitrovinyl groups. This is actually observed



\* The dipole moments of unsaturated nitro compounds have not been systematically determined.

\*\* For the reasons advanced above, in regard to the bond of the C=C group the O and phenylene can only be in trans-position 2.

The structure of the nitrovinyl group enables us to predict the following as possible configurations for (XI).

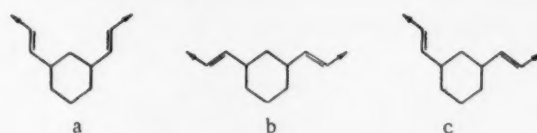


TABLE 1. Experimental Values of Dipole Moments (in debyes)

Compound	R = H			R = CH <sub>3</sub>			
	Compound no.	M.p., °C	$\mu$	Compound no.	M.p., °C	$\mu_1$	$\mu - \mu_1$
$\text{CH}_2 = \text{CHNO}_2$	I	T. кип. (4) 36°/100 mm	3,41	—	—	—	—
$\text{C}_6\text{H}_5 - \text{CH} = \text{C} \begin{smallmatrix} \text{NO}_2 \\ \text{R} \end{smallmatrix}$	II	58—59 (2)	4,51	II <sup>a</sup> (3)	65—66	4,14	-0,37
$\text{CH}_3 - \text{C}_6\text{H}_4 - \text{CH} = \text{C} \begin{smallmatrix} \text{NO}_2 \\ \text{R} \end{smallmatrix}$	III	101 (3)	5,00	III <sup>a</sup> (3)	52—53	4,55	-0,45
$\text{CH}_3\text{O} - \text{C}_6\text{H}_4 - \text{CH} = \text{C} \begin{smallmatrix} \text{NO}_2 \\ \text{R} \end{smallmatrix}$	IV	87 (4)	5,43	IV <sup>a</sup> (3)	43—44	5,09	-0,34
$(\text{CH}_3)_2\text{N} - \text{C}_6\text{H}_4 - \text{CH} = \text{C} \begin{smallmatrix} \text{NO}_2 \\ \text{R} \end{smallmatrix}$	V	184 (3)	7,61	V <sup>a</sup> (3)	123,5—124	7,18	-0,43
$\text{O}_2\text{N} - \text{C}_6\text{H}_4 - \text{CH} = \text{C} \begin{smallmatrix} \text{NO}_2 \\ \text{R} \end{smallmatrix}$	VI	206—207 (5)	1,00	VI <sup>a</sup> (10)	114—115	0,41	-0,59
$\text{C}_6\text{H}_5 - \text{CH} = \text{C} \begin{smallmatrix} \text{NO}_2 \\ \text{Br} \end{smallmatrix}$	—	—	—	VII <sup>a</sup> (11)	67—68	4,05	—
	VIII	75 (6)	5,00	VIII <sup>a</sup> (12)	74—75	4,59	-0,41
$\text{O}_2\text{NCH} = \text{CH} - \text{CH} = \text{CHNO}_2$	IX	147—148 (7)	0,71	—	—	—	—
$\text{O}_2\text{N} - \text{C}(\text{R}) = \text{CH} - \text{C}_6\text{H}_4 - \text{CH} = \text{C} \begin{smallmatrix} \text{NO}_2 \\ \text{R} \end{smallmatrix}$	X	231—232 (8)	1,05	X <sup>a</sup> (8)	122—123	1,65	±0,60
$\text{O}_2\text{N} - \text{C}(\text{R}) = \text{CH} - \text{C}_6\text{H}_3(\text{CH} = \text{C} \begin{smallmatrix} \text{NO}_2 \\ \text{R} \end{smallmatrix})$	XI	201—203 (9)	3,65	XI <sup>a</sup> (10)	108—109	64,20	±0,55

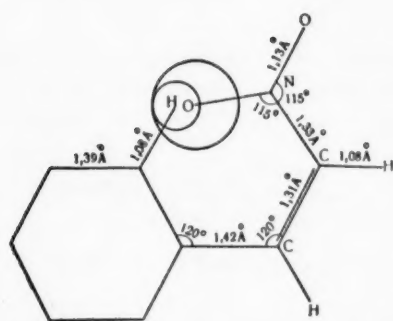


Fig. 1

Due to the irregularity of the  $\beta$ -nitrovinyl group, the angle between the moments of the nitrovinyl groups will in configuration a) be smaller than, in configuration b) greater than, and in configuration c) equal to  $120^\circ$ , while the over-all moment will be respectively greater than, smaller than, and equal to 4.3 D. Experiment gives a moment of 3.65 D which points to structure b) for 1,3-bis-( $\beta$ -nitrovinyl)benzene.

On the assumption of regularity of the nitrovinyl group in 1,3-bis-( $\beta$ -nitrovinyl)benzene (XII), its moment should be equal to 4.3 D, i.e., equal to the moment of nitrostyrene (4.51 D) less 0.2 D (in analogy to the case of m-dinitrobenzene (3.8 D) and nitrobenzene (4.01 D). Substitution of the methyl group for the hydrogen atom at the  $\beta$ -carbon of nitrostyrenes leads to lowering of the dipole moments by 0.4 D (II<sup>a</sup>-IX<sup>a</sup>, Table 1).

In  $\beta$ -methyl- $\beta$ -nitrostyrenes the coplanarity of the molecules is destroyed owing to the close packing of the atoms of the methyl group (van der Waals radius of  $\sim 2\text{\AA}$ ) at the  $\alpha$ -hydrogen of the benzene ring and the oxygen of the benzene ring and the oxygen of the nitro group (Fig. 2).

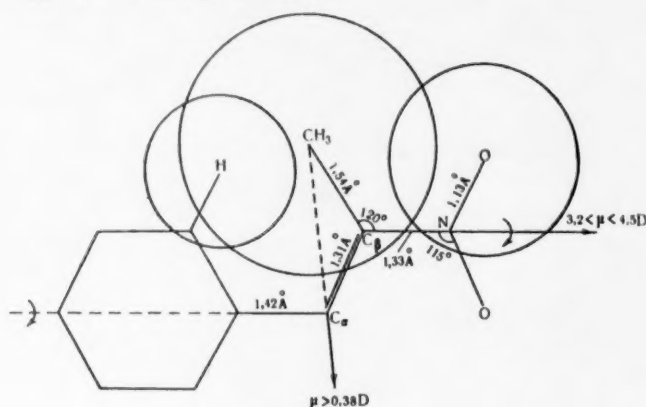


Fig. 2

A consequence of the loss of coplanarity is a weakening of the  $\pi$ -conjugation in  $\beta$ -methyl- $\beta$ -nitrostyrenes with participation of the benzene ring and the vinyl and nitro groups, although the less effective  $\pi, \sigma$ -conjugation of the C-H bonds of the methyl group and the double bonds of the vinyl residue is maintained. Since the magnitudes of the dipole moments are the result of vectorial addition of the moments of the individual polar bonds and groups and of the conjugated dipole moment, any weakening of conjugation naturally leads to lowering of the experimental dipole moments.

In 1,4- and 1,3-bis-(3-nitro- $\beta$ -methylvinyl)benzenes ( $X^a$  and  $XI^a$ ) the role of the moment resulting from  $\pi, \sigma$ -conjugation of the methyl group and the ethylenic residue becomes decisive; it is directed along the line of the  $C_\beta - CH_3$  bond with the positive end at the methyl group. The geometry of  $X^a$  and  $XI^a$  is similar to that of 1,4 and 1,3-bis-( $\beta$ -nitrovinyl)benzenes ( $X$  and  $XI$ ) which have *cis*-configuration relative to the benzene ring. The moment resulting from addition of the transverse components of the moments of the nitrovinyl groups is naturally greater than in the case of  $X$  and  $XI$ . The data are consistent with the results of measurements of the Raman spectra of aryl nitroalkenes [13].

The dipole moments ( $\mu$ ) in debyes were measured in benzene at  $25^\circ$  by the beat method, using the formula:

$$\mu = 0,0127 \sqrt{(P_\infty - P_E - P_A)T},$$

or, at  $298^\circ\text{K}$  using the formula:

$$\mu = 0,220 \sqrt{P_\infty - P_E - P_A},$$

where  $P_\infty$  = molar polarization of the substance at infinite dilution;  $P_E$  = electronic polarization;  $P_A$  = atomic polarization.

The electronic polarization is assumed equal to the molar refraction  $MR_D$  and is calculated additively as the sum of the refractions of atoms and bonds for the sodium D line; the atomic polarization was calculated by the additive rule derived by one of us [14], assuming the following group increments of  $P_A$ :  $\text{NO}_2$   $3.9\text{ cm}^3$ ,  $-\text{CH}=\text{CHNO}_2$   $7.9\text{ cm}^3$ ,  $\text{CH}_3$   $0.9\text{ cm}^3$ .

In two cases (compounds IV, V, XIV, and XV), when the value of  $P_A$  could not be calculated by this method,  $P_A$  was assumed equal to  $0.15 MR_D$  which is fully justified for large dipole moments.

The investigated compounds were synthesized by known procedures and thoroughly purified until the melting or boiling points were constant.



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# SYNTHESIS AND INVESTIGATION OF THE STRUCTURE OF DOUBLE DIAZONIUM SALTS OF ALUMINUM HALIDES

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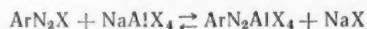
Systematic investigation of the infrared spectra of double diazonium salts of heavy metal chlorides in the 2100-2300  $\text{cm}^{-1}$  region led us to the conclusion that the valence vibration frequency of the  $\text{N}\equiv\text{N}$  triple bond ( $\nu_{\text{N}\equiv\text{N}}$ ) is a unique characteristic of these compounds which depends on the initial aryldiazonium salt, the metallic chloride, the valence of the metal, and the composition of the salt [1-3]. This enabled us to distinguish between complex mixtures of diazonium salts of thallium and bismuth of various compositions and to isolate analytically pure substances [2, 3].

Formation of double diazonium salts of heavy metal chlorides (Fe, Sb, Zn, Cd, Hg) always leads to lowering of the  $\nu_{\text{N}\equiv\text{N}}$  characterizing the original aryldiazonium chloride. This absorptive property of the  $\text{N}\equiv\text{N}$  triple bond suggested to us the possibility of a certain, probably weak, interaction between the metal atom and the nitrogen of the diazonium group [1]. We obtained confirmation of this hypothesis on the basis of a study of the ultraviolet spectra of double aryldiazonium salts of cobalt and copper chlorides [4].

We have now commenced a study of the infrared spectra of double diazonium salts of halides of light metals in which we cover not only the 2100-2300  $\text{cm}^{-1}$  region but also the 400-1500  $\text{cm}^{-1}$  region in which we can expect the appearance of absorption bands corresponding to the vibrations of light metal anions of the type of  $[\text{MeX}_n]^-$ .

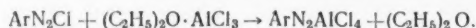
In this paper we describe the synthesis and investigation of the infrared spectra of double diazonium salts of aluminum chloride and bromide. These salts have not been described in the literature.

The methods developed for synthesis of double diazonium salts of heavy metals were found unsuitable for the preparation of double diazonium salts of aluminum chloride and bromide because water and alcohol, used as solvents, hydrolyzed aluminum halides with facility. The required objective was also not achieved by use of salts of the type of  $\text{NaAlX}_4$  in an exchange reaction



in place of aluminum halides.

We succeeded in preparing double diazonium salts of aluminum halides with the help of the etherates of the latter. In this case the reaction proceeds in accordance with the equation:



The resulting aryldiazonium aluminochloride dissolves in excess of the etherate and can be isolated in sufficiently pure form by precipitation with absolute ether. By means of this method we synthesized for the first time aryldiazonium aluminochlorides of the type of  $\text{p-XC}_6\text{H}_4\text{N}_2\text{AlCl}_4$ , where  $\text{X} = \text{CH}_3\text{O}$ ,  $\text{CH}_3$ ,  $\text{Br}$ ,  $\text{H}$ ,  $\text{NO}_2$ .

The new compounds are white or yellowish ( $\text{p-NO}_2\text{C}_6\text{H}_4\text{N}_2\text{AlCl}_4$ ), crystalline substances, insoluble in ether, benzene, carbon tetrachloride, and chloroform. They react energetically with water and alcohol with evolution of hydrogen chloride; they deliquesce in the air but are fairly stable when stored in dry air. An exception is  $\text{C}_6\text{H}_5\text{N}_2\text{AlCl}_4$  which begins to break down with loss of nitrogen even in the course of synthesis.

By analogous route we prepared aryldiazonium aluminobromides of the type of  $\text{p-XC}_6\text{H}_4\text{N}_2\text{AlClBr}_3$ , where  $\text{X} =$

= CH<sub>3</sub>O, CH<sub>3</sub>, Br, H, NO<sub>2</sub>, whose properties are similar to those of the aluminochlorides described previously. Aryldiazonium aluminiodides could not be prepared by this method (the reaction mixture decomposed with violence).

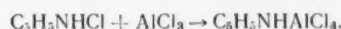
The infrared spectra of the aryldiazonium aluminochlorides and aluminobromides in the 2200-2300 cm<sup>-1</sup> and 400-600 cm<sup>-1</sup> regions are detailed in Tables 1 and 2.

TABLE 1. Frequencies of  $\nu_{N\equiv N}$  (cm<sup>-1</sup>) of Absorption Maxima of Diazonium Aluminohalides of the Composition  $p\text{-XC}_6\text{H}_4\text{N}_2\text{AlX}_4$  in the 2200-2300 cm Region

Anion	X				
	CH <sub>3</sub> O	CH <sub>3</sub>	Br	H	NO <sub>2</sub>
AlCl <sub>4</sub> <sup>-</sup>	2233	2255	2266	2270	2286
AlClBr <sub>3</sub> <sup>-</sup>	2227	2242	2262	2265	2279
Cl <sup>-</sup>	2248	2266	2278	2298	2294

Vibration frequencies of the corresponding diazonium chlorides are also given in Table 1 for comparison. Absorption bands of the N≡N triple bonds are observed in the 2200-2300 cm<sup>-1</sup> region for all the investigated compounds. Relative to the initial diazonium chlorides, the bands are lowered by 8 to 28 cm<sup>-1</sup> in the case of aluminochlorides and by 15 to 33 cm<sup>-1</sup> in the case of aluminobromides. The law that we established for double diazonium salts of heavy metals [1] is thus seen to apply to the spectra of double diazonium salts of aluminum halides in the 2200-2300 cm<sup>-1</sup> region.

Table 2 contains, apart from data for the absorption spectra of diazonium aluminochlorides, our data measured in the same region for diazonium chlorides, complexes of aluminum chloride with pyridine and trimethylamine, and also for KAICl<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>NHAICl<sub>4</sub>, and (CH<sub>3</sub>)<sub>3</sub>NHAICl<sub>4</sub>. The latter were prepared by the reaction:



We see from the tabulated data and the curves in Fig. 1 that the spectra of such ionic compounds as KAICl<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>NHAICl<sub>4</sub>, and (CH<sub>3</sub>)<sub>3</sub>NHAICl<sub>4</sub> are characterized by a very broad and strong band in the 550-400 cm<sup>-1</sup> region with maxima at 500-480 cm<sup>-1</sup>. This band is absent from complexes of aluminum chloride with pyridine and trimethylamine.

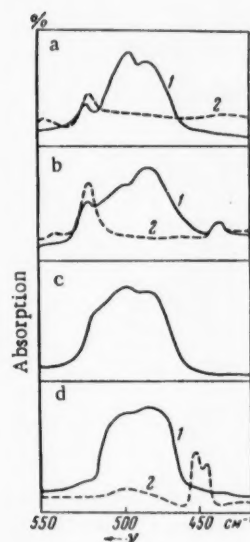


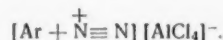
Fig. 1. Infrared absorption spectra in the 550-400 cm<sup>-1</sup> region. a)  $p\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2\text{AlCl}_4$  (1),  $p\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2\text{Cl}$  (2); b)  $p\text{-BrC}_6\text{H}_4\text{N}_2\text{AlCl}_4$  (1),  $p\text{-BrC}_6\text{H}_4\text{N}_2\text{Cl}$  (2); c) KAICl<sub>4</sub>; d) C<sub>6</sub>H<sub>5</sub>NHAICl<sub>4</sub> (1), C<sub>6</sub>H<sub>5</sub>N·AlCl<sub>3</sub> (2).

of aluminum halides were obtained by addition of the aluminum halide in small portions to cooled ether in an atmosphere of dry nitrogen.

The broad absorption band in the 550-440 cm<sup>-1</sup> region must consequently be assigned to the [AlCl<sub>4</sub>]<sup>-</sup> anion.

If the aryldiazonium aluminochlorides had an ionic structure, we should expect their spectra to contain the absorption band corresponding to the [AlCl<sub>4</sub>]<sup>-</sup> anion. All the aluminochlorides that we investigated did indeed contain a band at 500-580 cm<sup>-1</sup> whose form, strength, and position were similar to those of the band of KAICl<sub>4</sub> and other compounds with an ionic structure. In addition to the above-mentioned characteristic band, the spectra of aryldiazonium aluminochlorides contain absorption maxima at 520 cm<sup>-1</sup> (for all investigated compounds) and 440 cm<sup>-1</sup> (for  $p\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2\text{AlCl}_4$  and  $p\text{-BrC}_6\text{H}_4\text{N}_2\text{AlCl}_4$ ). These bands are characteristic of aryldiazonium chlorides (Table 2), while the broad and intense [AlCl<sub>4</sub>]<sup>-</sup> band is absent from the spectra of the latter.

The results support the hypothesis of an ionic structure of aryldiazonium aluminohalides:



We may therefore suggest that our observation of the systematic lowering of the triple bond frequency ( $\nu_{N\equiv N}$ ) on transition from aryldiazonium chlorides to aluminochlorides and in turn to aluminobromides is explicable in terms of the different influences of the Cl<sup>-</sup>, [AlCl<sub>4</sub>]<sup>-</sup>, and [AlClBr<sub>3</sub>]<sup>-</sup> anions on the N≡N triple bond.

#### EXPERIMENTAL

Aryldiazonium chlorides corresponding to aniline,  $p$ -toluidine,  $p$ -bromoaniline,  $p$ -nitroaniline, and  $p$ -anisidine were prepared by the Knoevenagel reaction and dried in a vacuum-desiccator over P<sub>2</sub>O<sub>5</sub>. Aluminum chloride was sublimed prior to use, and aluminum bromide and iodide were distilled in vacuo. Etherates

Aryldiazonium aluminochlorides and aluminobromides were prepared by addition of diazonium chloride to excess of the appropriate aluminum halide etherate at room temperature. The mixture was stirred for several minutes until the diazonium chloride had dissolved completely. The double salt was precipitated with absolute ether. The precipitate was washed four times with ether and dried in a vacuum-desiccator. In the case of  $C_6H_5N_2AlCl_4$  the diazonium chloride was added to aluminum chloride etherate cooled to  $-10^\circ$ . Analyses and melting points of the prepared compounds are set forth in Table 3.

TABLE 2. Absorption Spectra in the 400-600  $cm^{-1}$  Region

Compound	$\nu$ , $cm^{-1}$			
p- $CH_3OC_6H_4N_2AlCl_4$	520c	500пл	480c	
p- $CH_3C_6H_4N_2AlCl_4$	520c	500пл	480c	440cp
p- $BrC_6H_4N_2AlCl_4$	520c	500пл	484c	440cp
p- $NO_2C_6H_4N_2AlCl_4$	520cp	500c	484c	
p- $CH_3OC_6H_4N_2Cl$	518cp	494cp		
p- $CH_3C_6H_4N_2Cl$	520c			440cp
p- $BrC_6H_4N_2Cl$	516c			440cp
p- $NO_2C_6H_4N_2Cl$	518cp			
$KAlCl_4$		500c	484c	
$C_6H_5NHAICl_4$		500—480cm		
$(CH_3)_3NHAICl_4$		500—480cm		
$C_6H_5N \cdot AlCl_3$	452c	446cp		
$(CH_3)_3N \cdot AlCl_3$				

no. bands in the 600-400  $cm^{-1}$  region

Note: c = strong band; пл = broad; cp = medium; пл = shoulder.

TABLE 3

Compound	M.p., $^\circ C$	Empirical formula	C, %		H, %		N, % (diazo)	
			found	calc.	found	calc.	found	calc.
p- $CH_3OC_6H_4N_2AlCl_4$	72—73 *	$C_7H_7ON_2Cl_4Al$	27,29	27,66	1,53	1,33	9,30	9,22
p- $CH_3C_6H_4N_2AlCl_4$	82	$C_7H_7N_2Cl_4Al$	28,70	29,19	1,70	1,40	9,37	9,73
p- $BrC_6H_4N_2AlCl_4$	94—95	$C_6H_4N_2Cl_4BrAl$	19,68	20,52	1,87	1,14	7,69	7,94
$C_6H_5N_2AlCl_4$	63—65	$C_6H_5N_2Cl_4Al$					8,75	10,2
p- $NO_2C_6H_4N_2AlCl_4$	95	$C_6H_4O_2N_2Cl_4Al$	22,47	22,58	1,52	1,26	8,85	8,78
p- $CH_3OC_6H_4N_2AlClBr_3$	97—98 *	$C_7H_7ON_2Cl_3Br_3Al$					6,38	6,40
p- $CH_3C_6H_4N_2AlClBr_3$	92—93	$C_7H_7N_2Cl_3Br_3Al$					6,40	6,64
p- $BrC_6H_4N_2AlClBr_3$	104—105	$C_6H_4N_2Cl_3Br_4Al$					5,51	5,76
$C_6H_5N_2AlClBr_3$	76—78	$C_6H_5N_2Cl_3Br_3Al$					6,83	6,87
p- $NO_2C_6H_4N_2AlClBr_3$	65	$C_6H_4O_2N_2Cl_3Br_3Al$					5,97	6,19

\* The substance melts; the other substances decompose.

The infrared spectra of the compounds in the 2100-2300  $cm^{-1}$  region were measured with the IKS-11 spectrophotometer with a lithium fluoride prism; the spectra in the 400-680  $cm^{-1}$  region were measured with the IKS-14 spectrophotometer with a potassium bromide prism.

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# REACTION OF ALKYL- AND ALKOXYOXAZOLES WITH MALEIMIDE

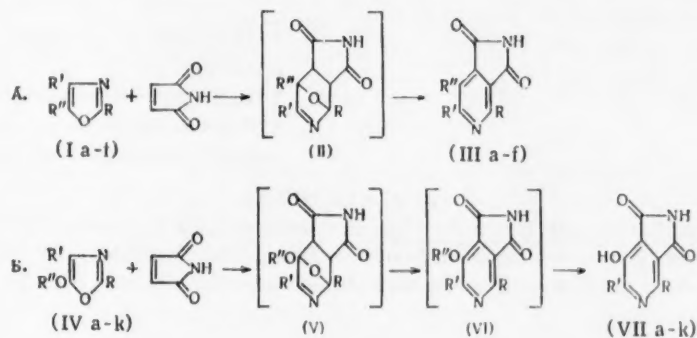
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In earlier papers [1,2] we described the condensation of some oxazole derivatives with maleic acid and its anhydride. These commonly employed philodienes showed good activity in reactions with alkyl- and alkoxyalkyloxazoles but they did not react with oxazoles substituted by electron-accepting groups (2-phenyl-5-ethoxy-, 2-ethyl-5-ethoxyoxazoles). In these cases maleimide showed greater activity. The imide has been little used in the diene synthesis but is evidently a very reactive substance [3-7]. Its condensation with alkyl- and alkoxyoxazoles proceeds with good yields and with very much greater facility than the reaction with maleic anhydride. The end products of conversion of oxazoles are imides of substituted pyridine-3,4-dicarboxylic acids and in some cases the half amides of these acids:



In no case were the intermediate epoxytetrahydropyridinic derivatives II and V detected. Just as in the reaction with maleic anhydride, alkoxyoxazoles directly give not the pyridinic ethers VI but the corresponding hydroxy compounds.

The complete results of the investigation are set forth in Tables 1 and 2. Yields of adducts obtained in the reaction with maleic anhydride are also shown for comparison.

The high activity of maleimide in reactions with oxazoles is reflected in the fact that it reacts with very much greater speed than maleic anhydride. Appreciable heat is released when oxazoles are mixed with the imide, and the adduct starts to come down after only 10-30 min. In the series of alkylloxazoles (I a-e) the yields of III a-e 50-98%, i.e., 20% higher than the yields achieved in the reaction with maleic anhydride. The high yield of 5-tert-butyloxazole-3,4-dicarboximide (III f) is interesting because 4-tert-butyloxazole (I f) does not react with maleic anhydride. All the alkoxyoxazoles, except the first members of the homologous series (IV a and IV h), give high yields of adducts VII a-k in condensation with maleimide irrespective of the length of the alkyl chain in the 2 position and of the presence of a substituent in the 4 position. 2-Phenyl-5-ethoxyoxazole (I g) and its vinyllog-2-styryl-5-ethoxyoxazole-do not enter into reaction with the anhydride but undergo condensation with maleimide without difficulty.

The structure of the reaction products was confirmed by alternative synthesis of some of the pyridinedicarboximides (III a-e) by heating of the corresponding free pyridine-3,4-dicarboxylic acids with urea in ethylene glycol.



In some condensation experiments with Ig, only the product of partial hydrolysis of the cyclic imide ring—2,5,6-trimethyl-3(or 4)-carbamyloxy-4(or 3)-carboxylic acid—was isolated (infrared spectrum  $\lambda_{\max}$  1590, 3152-3176  $\text{cm}^{-1}$ ) ( $\text{CONH}_2$ ). Oximide VII i formed from IV i was converted during recrystallization from methanol into 2-ethyl-6-methyl-5-hydroxy-4(or 3)-carbomethoxy-3(or 4)-carbamyloxy-4(or 3)-carboxylic acid (infrared spectrum  $\lambda_{\max}$  1710-1730  $\text{cm}^{-1}$ ) ( $\text{COOR}$ ; 1637  $\text{cm}^{-1}$ ) ( $\text{CONH}_2$ ). Data for the structure of the adduct of oxazole IV g will be published later.

The authors are deeply grateful to Academician B. A. Kazanskii for his close interest in this work.

TABLE 1. Reaction of Alkylloxazoles with Maleimide (Scheme A)

I-III	R	R'	R''	Yield of III, %	Yield of maleic anhydride adduct, %
a	H	CH <sub>3</sub>	CH <sub>3</sub>	93	85
b	CH <sub>3</sub>	CH <sub>3</sub>	H	98	78
c	CH <sub>3</sub>	H	CH <sub>3</sub>	81,9	80
d	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	49,5	52
e	CH <sub>3</sub>	—(CH <sub>2</sub> ) <sub>4</sub> —		54,5	35
f	H	(CH <sub>3</sub> ) <sub>3</sub> C	H	64,3**	0

\* In some experiments 2,5,6-trimethyl-3(or 4)-carbamyloxy-4(or 3)-carboxylic acid was isolated; yield 93.6%.

\*\* Half amide of the acid.

TABLE 2. Reaction of 5-Alkoxyoxazoles with Maleimide (Scheme B)

VII IV	R	R'	R''	Yield of VII, %	Yield of adduct from maleic anhydride, % [2]
a	CH <sub>3</sub>	H	C <sub>2</sub> H <sub>5</sub>	43	54
b	C <sub>2</sub> H <sub>5</sub>	H	C <sub>2</sub> H <sub>5</sub>	80	47
c	n-C <sub>3</sub> H <sub>7</sub>	H	C <sub>2</sub> H <sub>5</sub>	77	31,5
d	n-C <sub>4</sub> H <sub>9</sub>	H	C <sub>2</sub> H <sub>5</sub>	82,8	42,3
e	n-C <sub>5</sub> H <sub>11</sub>	H	C <sub>2</sub> H <sub>5</sub>	81,4	40
f	C <sub>6</sub> H <sub>5</sub>	H	C <sub>2</sub> H <sub>5</sub>	43,5	0
g	C <sub>6</sub> H <sub>5</sub> CH=CH	H	C <sub>2</sub> H <sub>5</sub>	70*	0
h	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	36	36
i	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	72,6**	25
j	n-C <sub>5</sub> H <sub>11</sub>	CH <sub>3</sub>	CH <sub>3</sub>	68	15,8***
k	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	84,8	0

\* The structure of the adduct will be described separately.

\*\* Half amide of the acid.

\*\*\* Maleic anhydride was condensed with 2-n-amyloxy-4-methyl-5-ethoxyoxazole.

#### EXPERIMENTAL

**5,6-Dimethylpyridine-3,4-dicarboximide (IIIa).** A mixture of 0.8 g of 4,5-dimethyloxazole, 0.8 g of maleimide, and a small quantity of hydroquinone was heated for 2 hr in 5 ml of benzene. The crude reaction product melted at 263-265°. After sublimation in vacuo IIIa had m.p. 268-270°; a mixture with the product of alternative synthesis had m.p. 268-270°.

**2,6-Dimethylpyridine-3,4-dicarboximide (IIIb)** was prepared from 2.0 g of 2,4-dimethyloxazole and 2.0 g of maleimide. M.p. 224-226° (from acetone); m.p. of mixture with product of alternative synthesis 224°.

**2,5-Dimethylpyridine-3,4-dicarboximide (IIIc)** was prepared similarly to IIIa; m.p. 271-272°. M.p. of mixture with product of alternative synthesis 271-272°.

**2,5,6-Trimethylpyridine-3,4-dicarboximide (IIId).** A mixture of 2.2 g of 2,4,5-trimethyloxazole and 2.1 g of maleimide was heated in benzene in presence of hydroquinone for 2 hr. M.p. of precipitate 220-221°. M.p. of mixture with product of alternative synthesis 220°.

**2,5,6-Trimethyl-3(or 4)-carbamyloxy-4(or 3)-carboxylic acid.** A mixture of 4.2 g of 2,4,5-trimethyloxazole and 3.6 g of maleimide was heated in a mixture of benzene and xylene (1:1) for 1.5 hr. The precipitated amidoacid melted at 180°; a pure sample had m.p. 183.5-185.5° (from acetone + ligroine and then from acetone). Found %: C 57.95, 58.16; H 5.55, 5.72.  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$ . Calculated %: C 57.68; H 5.77.

**2-Methyl-5,6-tetramethylenepyridine-3,4-dicarboximide (IIIe).** From 2.0 g of 2-methyl-4,5-tetramethylenoxazole and 1.5 g of maleimide, with boiling in benzene for 4 hr. M.p. of precipitate 246-247°. M.p. of mixture with product of alternative synthesis 245-246°.

**5-Tert-butyl-3(or 4)-carbamyloxy-4(or 3)-carboxylic acid.** Reaction components were 2.0 g of 5-tert-butylloxazole and 2.75 g of maleimide (heating in benzene + hydroquinone for 3 hr). The precipitate was separated. The filtrate was boiled for 5 hr, and evaporated; the residue was washed with water. M.p. 176° after recrystallization from ethyl acetate and a mixture of acetone and hexane. Found %: C 59.64, 59.38; H 6.31, 6.19.  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_3$ . Calculated %: C 59.43; H 6.36.

2-Methyl-5-hydroxypyridine-3,4-dicarboximide (VIIa). Reaction components were 4 g of 2-methyl-5-ethoxyoxazole and 3.6 g of maleimide (heated in 10 ml of benzene + hydroquinone for 1.5 hr). The crude adduct melted at 273°; after purification it had m.p. 308° (from alcohol + benzene). Found %: 54.01, 53.89; H 3.40, 3.50.  $C_8H_6N_2O_3$ . Calculated %: C 53.93; H 3.39.

2-Ethyl-5-hydroxypyridine-3,4-dicarboximide (VIIb). A mixture of 3.0 g of 2-ethyl-5-ethoxyoxazole and 2.2 g of maleimide was heated in 10 ml of benzene (with pyrogallol) for 4 hr. M.p. of adduct 254°. The pure preparation had m.p. 258° (from methanol + benzene). Found %: C 56.44, 56.50; H 4.13, 4.00.  $C_9H_8N_2O_3$ . Calculated %: C 56.25; H 4.18.

2-n-Propyl-5-hydroxypyridine-3,4-dicarboximide (VIIc). From 2.0 g of 2-n-propyl-5-ethoxyoxazole and 1.4 g of maleimide in 10 ml of benzene (with pyrogallol); heating for 3 hr. M.p. of precipitate 247-250°. M.p. after purification 251-252° (from acetone-benzene and methanol-benzene). Found %: C 58.03, 53.23; H 4.76, 4.86.  $C_{10}H_{10}N_2O_3$ . Calculated %: C 58.24; H 4.89.

2-n-Butyl-5-hydroxypyridine-3,4-dicarboximide (VIIId). Prepared similarly to VIIb from 2.5 g of 2-butyl-5-ethoxyoxazole and 1.7 g of maleimide. M.p. of crude adduct 232°; m.p. of pure specimen 234.5-235° (from methanol-benzene, acetone-benzene). Found %: C 60.37, 60.44; H 5.67, 5.64.  $C_{11}H_{12}N_2O_3$ . Calculated %: C 59.98; H 5.49.

2-n-Amyl-5-hydroxypyridine-3,4-dicarboximide (VIIe). Prepared by boiling 3.7 g of 2-amyl-5-ethoxyoxazole and 1.95 g of maleimide in toluene with hydroquinone for 4 hr. The solution was evaporated to dryness. M.p. of adduct 231°; m.p. of pure preparation 234° (from alcohol, then from acetone). Found %: N 12.52, 12.53.  $C_{12}H_{14}N_2O_3$ . Calculated %: N 11.96.

2-Phenyl-5-hydroxypyridine-3,4-dicarboximide (VIIf). 2-Phenyl-5-ethoxyoxazole (3.6 g) was heated with maleic anhydride (2.0 g) for 3 hr in xylene (containing hydroquinone). M.p. of unpurified product 279-282°. The pure preparation had m.p. 286-287° (from methanol-benzene). Found %: C 64.36; H 3.33.  $C_{13}H_{10}N_2O_3$ . Calculated %: C 65.00; H 3.36.

2,6-Dimethyl-5-hydroxypyridine-3,4-dicarboximide (VIIh) was prepared similarly to VIIc from 2.3 g of 2,4-dimethyl-5-methoxyoxazole and 1.8 g of maleimide. M.p. 275-277° (from alcohol-benzene-methylethyl ketone). Found %: C 56.62, 56.74; H 4.16, 4.13.  $C_9H_8N_2O_3$ . Calculated %: C 56.25; H 4.19.

2-Methyl-6-ethyl-5-hydroxypyridine-3,4-dicarboximide (VIIk). From 3.1 g of 2-methyl-4-ethyl-5-ethoxyoxazole and 1.95 g of maleimide by boiling in toluene for 6 hr. M.p. of crude adduct 225°; after sublimation and recrystallization from benzene m.p. 255-257°. Found %: N 13.52, 13.65.  $C_{10}H_{10}N_2O_3$ . Calculated %: N 13.56.

2-Ethyl-6-methyl-5-hydroxy-4(or 3)-carbamiypyridine-3(or 4)-carboxylic acid. From 2.0 g of 2-ethyl-4-methyl-5-methoxyoxazole and 1.5 g of maleimide in benzene by boiling for 4 hr. M.p. 157° (from methanol-benzene, acetone-benzene). Found %: 55.41, 55.52; H 6.17, 6.22.  $C_{11}H_{14}N_2O_4$ . Calculated %: C 55.45; H 5.92.

Reaction of 2-styryl-5-ethoxyoxazole with maleimide. 2-Styryl-5-ethoxyoxazole (4.2 g) and 2.1 g of maleimide were boiled in xylene solution for an hour. The melting point of the precipitate (washed with ether) was 245°. After purification the adduct had m.p. 268-268.5° (from acetone-benzene and methanol-benzene). Found %: C 62.16, 62.42; H 4.75, 4.60.  $C_{15}H_{12}N_2O_4$ . Calculated %: C 61.76; H 4.46.

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# INVESTIGATION OF THE COMPOSITION OF PRODUCTS OF REACTION OF VANADIUM OXYTRICHLORIDE WITH TRIETHYLALUMINUM

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Complex organometallic catalysts prepared on the basis of titanium salts and alkylaluminums are largely employed for stereospecific polymerization of diolefinic hydrocarbons since these catalyst systems lead to *cis*-1,4-polyisoprene and *cis*-1,4-polybutadiene. Vanadium-containing catalysts have been used, for example, for copolymerization of ethylene and propylene. Polymerization of diethylenic hydrocarbons gives polymers containing 90-95% of monomer units with *trans*-1,4-orientation, so that a route is opened up to the synthesis of gutta-percha. Catalysts on the basis of vanadium salts moreover possess a simpler and more stable structure than catalysts on the basis of titanium salts, so that they are convenient for a detailed study of the mechanism of catalytic polymerization. The composition and catalytic properties of catalysts prepared on the basis of vanadium chlorides were studied by Natta and co-workers [1-6]. They established the formation of a precipitate mainly consisting of complex compounds of vanadium chlorides with alkylaluminums (1:1 molar ratio) on reduction of vanadium oxytrichloride with alkylaluminums. The chlorine content of the precipitate decreases with increasing initial ratio of alkylaluminum to vanadium oxytrichloride. The objective of the present investigation was to derive the laws enabling calculation of the quantitative composition of the products of reaction of vanadium oxytrichloride with triethylaluminum.

Reaction was effected by addition of 0.1 M benzene solution of triethylaluminum to 0.1 M solution of vanadium oxytrichloride at 20° under conditions excluding the presence of traces of moisture and oxygen. In one series of experiments the precipitate was filtered off and washed several times with benzene. It was then dissolved in 2% sulfuric acid and titrated with 0.1 N permanganate for determination of the average valence of the vanadium. The chlorine content was then determined by the Volhard method, that of aluminum by the Paulson method [8], and that of vanadium by reduction with sulfur dioxide [7]. The benzene solution obtained after the precipitate had been filtered off was analyzed in the same way. In another series of experiments the gaseous hydrocarbons evolved in the reaction (ethane, ethylene, butane)\* were collected. The number of ethyl groups of the triethylaluminum which had reacted with formation of gaseous hydrocarbons was estimated from the quantity of carbon dioxide formed on combustion of the gas mixture over copper oxide. It was assumed that the intermediate unstable organovanadium compounds are decomposed substantially completely [9] and that polymerization of ethylene does not play an important part. Consequently the number of such groups should be equivalent to the amount of diethylaluminum chloride formed. After the hydrocarbon gases had been removed, the reaction mixture was treated with 2% sulfuric acid, and the number of ethyl groups not participating in the reaction was estimated from the volume of ethane evolved. The quantities of diethylethoxyaluminum formed and of unreacted triethylaluminum were calculated on the basis of the data obtained.

It was found that the average valence of the vanadium in the reaction products decreases with increasing  $[Al(C_2H_5)_3]/[VOCl_3]$  molar ratio ( $\bar{n}$ ) when  $\bar{n}$  is less than 2 (Fig. 1). At the same time the quantity of diethylaluminum chloride and diethylethoxyaluminum formed increases (Fig. 2). For values of  $\bar{n} \geq 2$  the valence of the vanadium reaches a constant value. The reduction of vanadium therefore proceeds simultaneously in two directions.

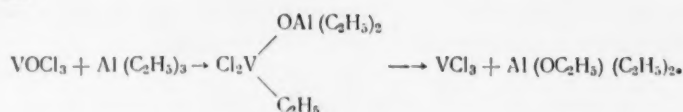
1) At the V-Cl bond, i.e., in accordance with the scheme proposed by Jilman, Jones, and Woods [10]:



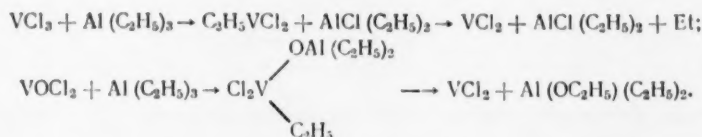
\* The composition of the gas mixture was not investigated.

where Et is ethylgroups calculated in the form of gaseous hydrocarbons.

2) At the V=O bond:



The resulting tri- and tetravalent vanadium compounds are further reduced in presence of excess of triethylaluminum:



Hence, the formation of one mole of diethylaluminum chloride leads to the vanadium valence being lowered by one, while in the formation of one mole of diethylethoxyaluminum the valence is lowered by two. The values of average valence of vanadium calculated from the quantity of diethylaluminum chloride and diethylethoxyaluminum formed are in satisfactory agreement with the values formed by direct titration (Fig. 1).

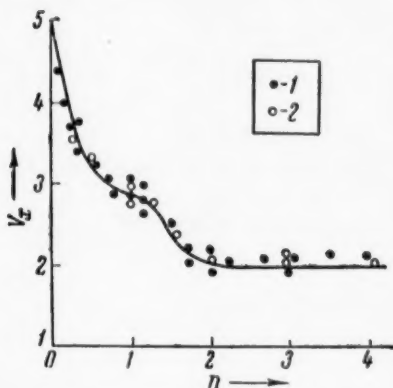


Fig. 1. Average valence of reduced vanadium ( $V_x$ ) as a function of  $\bar{n} = \text{Al}(\text{C}_2\text{H}_5)_3/\text{VOCl}_3$ : 1) On the basis of determination of content of diethylaluminum chloride and diethylethoxyaluminum in reaction products.

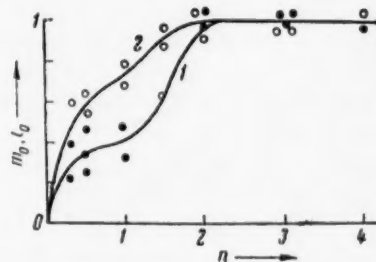


Fig. 2. Relation between content of diethylaluminum chloride ( $m_0$ ) and diethylethoxyaluminum ( $l_0$ ) in reaction products on magnitude of  $\bar{n} = \text{Al}(\text{C}_2\text{H}_5)_3/\text{VOCl}_3$  (in moles/mole  $\text{VOCl}_3$ ). 1) Content of diethylaluminum chloride; 2) content of diethylethoxyaluminum.

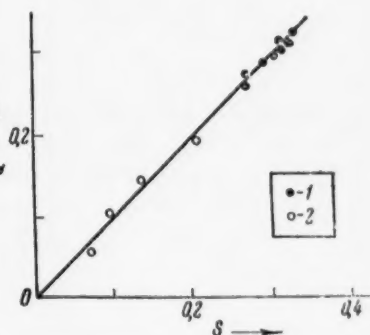


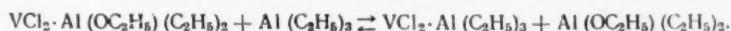
Fig. 3. Relation between  $Q$  and  $S$ : 1) When  $l_0 = 1$ ,  $m_0 = 1$ ; 2) when  $l_0 = 1$ ,  $m_0 > 1$ .

In the case of values of  $\bar{n} < 2$ , due to the high reactivity of vanadium oxytrichloride it is necessary to take also into account the reduction of the latter by the diethylaluminum chloride and diethylethoxyaluminum.

In the present communication we consider the simplest system formed with values of  $\bar{n}$  in the region of  $\bar{n} > 2$ . The insoluble complex compounds formed during reduction consist of equimolar quantities of vanadium chlorides and alkylaluminums. These compounds can evidently exist in equilibrium with the dissolved alkylaluminums. When  $\bar{n} > 2$ , the chlorine content of the solution above the precipitate increases with increasing  $\bar{n}$  (Table 1). Since no further reduction of vanadium then takes place, the increased content of chlorine is evidently due to the existence of the equilibrium:



A similar reaction may also be proposed in the case of diethylethoxyaluminum:



We use the following notation:  $\underline{m}_0, l_0$  are respectively the total content of diethylaluminum chloride and diethylethoxyaluminum in the reaction products;  $\underline{m}, l$  are respectively the content of the same component in the solution above the precipitate;  $\underline{m}_1, l_1$  are, respectively, the amounts of the same substances chemisorbed at the surface of the precipitate.\* If the particles of precipitate are small, we may write:

$$m_0 = m + m_1; l_0 = l + l_1$$

The equilibrium reaction constants will then have the following form:

$$K_1 = \frac{m}{m_1} \cdot \frac{1 - m_1 - l_1}{(n-1) - m - l};$$

$$K_2 = \frac{l}{l_1} \cdot \frac{1 - m_1 - l_1}{(n-1) - m - l}.$$

We can put

$$K_1 = K_2 = K$$

if the energies of formation of the complex compounds  $VCl_2, AlCl(C_2H_5)_2$  and  $VCl_2 \cdot Al(OC_2H_5)(C_2H_5)_2$  only differ slightly. Eliminating  $l$ , we obtain:

$$\left[ \frac{m_0}{(m_0 + l_0)(m_0 + m)} \right] = K \left[ \frac{m_0}{(m_0 + l_0)(m_0 + m)} \cdot \frac{(n-1)(m_0 - m)}{m} \right] + [1 - K].$$

A special series of experiments was run to verify the accuracy of the derived equation in a wide range of values of  $\underline{m}_0$ . In these experiments, after completion of the reaction of vanadium oxytrichloride with triethylaluminum, addition was made of diethylaluminum chloride or triethylaluminum, and the change in the chlorine content of the solution above the precipitate was determined. Experimental points in the coordinate system

$$Q = \left[ \frac{m_0}{(m_0 + l_0)(m_0 + m)} \right] \text{ and } S = \left[ Q \cdot \frac{(n-1)(m_0 - m)}{m} \right]$$

fall satisfactorily round a straight line passing through the origin of the coordinates (Fig. 3). Consequently,  $K = 1$ .

TABLE 1. Composition of Products of Reaction of Vanadium Oxytrichloride in Dependence on  $\underline{n} - [Al(C_2H_5)_3] / [VOCl_3]$

n	Composition of insoluble precipitate, g-atom/mole VOCl <sub>3</sub>			Composition of solution over precipitate, g-atom/mole VOCl <sub>3</sub>		
	V	Al	Cl	V	Al	Cl
0,20	0,59	0,20	1,80	0,40	Not detected	1,20
0,25	0,73	0,25	2,20	0,24	»	0,69
0,33	0,96	0,33	2,78	Not detected	»	Not detected
0,50	1,00	0,50	2,84	»	»	»
1,00	0,97	1,00	2,89	»	»	»
1,64	1,05	1,02	2,60	»	0,62	0,28
2,00	0,98	1,06	2,48	»	0,94	0,49
2,35	1,02	1,01	2,23	»	1,34	0,58
3,00	0,99	1,10	2,22	»	1,90	0,65
3,50	0,89	1,05	2,19	»	2,45	0,70
4,00	0,94	0,86	2,12	»	3,14	0,76
5,00	0,96	1,10	2,14	»	3,90	0,81
5,80	1,06	1,09	2,09	»	4,71	0,85
7,00	0,88	1,13	2,04	»	5,87	0,87

The results enable us to derive simple expressions for the quantities of diethylaluminum chloride and diethylethoxyaluminum in complex combination. When  $K_1 = K_2 = 1$ , it follows from the expressions for the equilibrium constants that:

$$m_1 = \frac{m_0}{n}, l_1 = \frac{l_0}{n}.$$

Consequently, the quantity of diethylaluminum chloride chemisorbed on the surface of the reduced vanadium chlo-

\*Amounts are expressed in moles per mole of initial vanadium oxytrichloride.



rides is inversely proportional to the quantity of triethylaluminum introduced into the reaction. A number of authors [1-5] have observed a fall in catalytic activity of catalysts of this type with increasing  $\text{AlR}_3/\text{VOCl}_3$  ratio. This can be explained as the result of lowering of the content of diethylaluminum chloride in complex combination if we assume that it is the active center for polymerization initiation. A detailed study of the influence of the composition of such catalysts of the kinetics of polymerization of diolefinic hydrocarbons will be the subject of later communications.

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# SYNTHESIS OF CARBOXYLIC ACIDS AND THEIR ESTERS FROM CARBON MONOXIDE AND ALCOHOLS WITH ACID CATALYSTS

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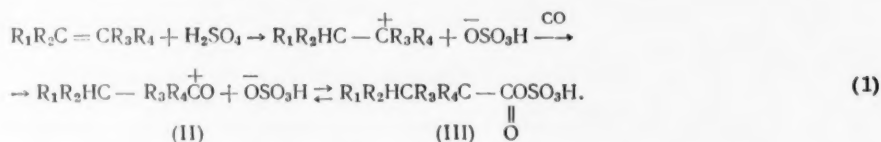
(Presented by Academician B. A. Kazanskii June 26, 1961)

Translated from Doklady Akademii Nauk SSSR, Vol. 141, No. 3,

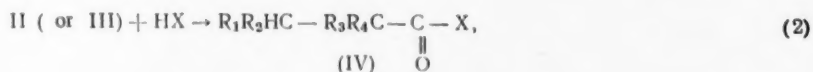
pp. 636-637, November, 1961

Original article submitted May 21, 1961

Carboxylic acids and esters of branched structure can be synthesized under relatively mild conditions in good yields by carboxylation [1] or carbalkoxylation [2], respectively, of olefins with carbon monoxide. The synthesis occurs in two stages. Initially an intermediate compound, having the character of an acylsulfuric acid, and entering an equilibrium with an acylcarboxylic acid and hydrosulfate ion, is formed from the olefin and carbon monoxide with catalyst participation (concentrated sulfuric acid) (at pressures to 90 atm).



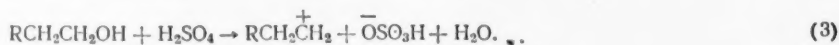
Then the carboxylic acid or its ester is formed by reaction with water or alcohol:



where  $X = OH$  or  $OR$ .

This process is accompanied by skeletal isomerization so that the main reaction products are in the form of isomer (IV).

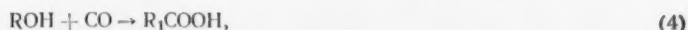
From reaction (1) it is apparent that the initial reagent is a carbonium ion in nature (I). Consequently, it is possible to suppose that other compounds which form carbonium ions similarly with sulfuric acid, in particular alcohols, can be used instead of olefins in reaction (1):



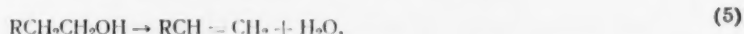
Therefore it was of interest to clarify whether alcohols could be substituted for olefins in the above process. The results of Koch and Haaf [3] showed the complete feasibility of such a process; these results showed that alcohols as well as olefins were converted under atmospheric pressure into carboxylic acids on reaction with formic acid in the presence of a large excess of sulfuric acid. It should be noted that in the literature data [4] high temperature and very high pressures (to 1000 atm) were used for a one-step synthesis of carboxylic acids from alcohols and carbon-monoxide.

In this study it was shown that intermediate compounds, later converted by reaction with water or alcohols to branched carboxylic acids or corresponding esters, were formed at increased pressure and room temperature from alcohols and carbon monoxide in the presence of sulfuric acid as catalyst. In this synthesis and in the case using olefins, the acids formed primarily have one more carbon atom in their molecules than the starting alcohol and a quaternary (thrice substituted) carbon atom in the position  $\alpha$  to the carboxyl group. This synthesis can be represented

formally as addition of carbon monoxide to the alcohol with simultaneous isomerization of the hydrocarbon radical of the alcohol



where  $\text{R}_1$  is a more branched radical than  $\text{R}$  with the same number of carbon atoms. However the chemistry of this first stage of the process can either be supposed as dehydration of the alcohol into olefin:



which then reacts according to equations (1) and (2), or as direct conversion of the alcohol into carbonium ions by reaction (3). The second route is more probable. This, in particular, agrees with the data of Koch and Haaf [4], according to which the carboxylic acid is obtained in good yields by reaction of certain alcohols, for example, neopentyl, which can not be directly dehydrated into olefins by reaction (5), with formic acid at atmospheric pressure in the presence of excess sulfuric acid.

The synthesis of acids and their esters was conducted thus: in the first step the alcohol, carbon monoxide, and sulfuric acid (d 1.84) were reacted at 60-90 atm; in the second step excess water or methanol was added to the reaction mixture. In the first case a carboxylic acid was obtained, in the second methyl ester with admixed carboxylic acid. Thus a mixture of acids in 70-80% yields was obtained from n-butyl or iso-butyl alcohol by addition of water to the reaction mass in the second step; by adding methanol, a mixture of esters and acids (in the weight ratio 5:1) was obtained with a total yield of about 60%. The main reaction products were: with n-butyl alcohol,  $\alpha$ -methylbutyric acid or the corresponding ester; with isobutyl alcohol, trimethylacetic acid or its ester. These compounds comprised 85-90% of the mixture of reaction products.

Thus, reaction of alcohols with carbon monoxide, as a result of which branched carboxylic acids or their esters\* are formed, occurs under relatively mild conditions.

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\* After completion of this work, an American patent [6] in which was described the synthesis of carboxylic acids from alcohols and carbon monoxide under analogous conditions, became accessible to the authors.

# PREPARATION OF 2,2-DISUBSTITUTED 1-AMINOINDAN-3-ONES

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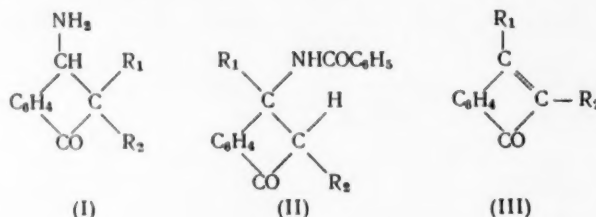
Institute for Organic Synthesis, Academy of Sciences, Latvian SSR

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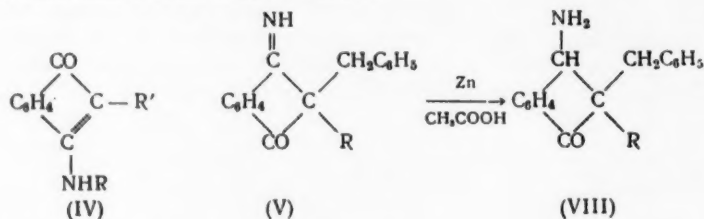
A large number of indane derivatives containing amino groups on the five-membered ring are known. Some of these compounds belong to the class of 2-aminoindan-1, 3-diones studied at length by many authors, for example [1-4]. 1-Aminoindanes [5-9], 1,3-diaminoindanes [10], 1-aminoindan-2-ols [11] and 2-aminoindan-1-ols [12] are also well known. The majority of these compounds have definite physiological activity. Thus it was of interest to obtain 1-aminoindan-3-ones (I), substances belonging to the indane  $\beta$ -aminoketone series. No data on the syntheses of these compounds could be found in the literature. Only some N-benzoyl derivatives of 1-aminoindan-3-ones (II) [13, 14] were obtained.



For (II) and (III): a)  $R_1 = H$ ;  $R_2 = C_6H_5$ . b)  $R_1 = C_6H_5$ ;  $R_2 = C_6H_5$ . v)  $R_1 = C_6H_5$ ;  $R_2 = CH_3$ . It was impossible to obtain any free 1-aminoindan-3-ones from them. Compound II underwent hydramine cleavage very easily, forming the corresponding 2,3-disubstituted indone III or further conversion products.

Reduction of 3-aminoindones IV also took place but did not lead to the intended or anticipated products (I,  $R_2 = H$ ) which must be unstable. It is probable that only 2,2-disubstituted 1-aminoindan-3-ones would be stable since they do not contain an easily cleaved hydrogen atom in the 2 position of the five-membered ring.

In connection with this we found that by reduction of 2,2-disubstituted 1-aminoindan-3-ones (V) [13, 15] the anticipated 1-aminoindan-3-ones (VII) were obtained, granted in low yields. The reduction was carried out on 1-iminoindan-3-one hydrochlorides (VI) which are easily obtained from the corresponding 3-aminoindones (IV) and the initial  $\beta$ -iminoketones (V) were formed in the reaction mixture.



For (V)–(VII) a)  $R = CH_3$ ; b)  $R = C_6H_5$ .

Tentative experiments showed that 1-aminoindan-3-ones are also formed by reduction of other 2,2-disubstituted 1-iminoindan-3-ones.

2,2-Disubstituted 1-aminoindan-3-ones are colorless substances readily soluble in common organic solvents and give all the reactions characteristic of primary amine group. They were characterized as their acetyl or phthaloyl derivatives and as their salts. The carbonyl group was demonstrated spectroscopically (see Table 1).

TABLE 1. IR Absorption Spectra of the 1-Aminoindan-3-ones Obtained

Compound	Benzene absorption	$\nu_{C=O}$	$\delta_{NH_3^+}$	$\nu_{NH_2}$ or $\nu_{NH_3^+}$
VIIa	1492 (44) 1607 (68)	1700 (95)	—	3292 (61) 3350 (64)
VIIb	1494 (40) 1604 (49)	1704 (88)	—	3337 (40) 3400 (40)
VIIb amine hydrochloride	1494 (60) 1604 (73)	1717 (90)	1530 (67) 1633 (53)	3443 (75) 3475 (70) p

According to the literature data solid indan-1-one has a carbonyl peak at  $1698\text{ cm}^{-1}$  [16]; in different solvent media this value increases noticeably (indan-1-one  $1710\text{ cm}^{-1}$  [17],  $1721\text{ cm}^{-1}$  [18],  $1708\text{ cm}^{-1}$  [19], 2-ethylindan-1-one  $1710\text{ cm}^{-1}$  [17]. For the amine hydrochloride (VIIb) the appearance of two new peaks is interesting:  $1530$  and  $1633\text{ cm}^{-1}$ . On one hand this can be the frequency for covalent N-H bond deformation of the amine group; on the other hand the oscillation  $\nu_{NH_3^+}$  is not observed above  $3200\text{ cm}^{-1}$  [20]. In this case we still find final assignment of frequencies difficult.

The succinate salt of amine VIIa, as expected, exhibited marked antispasmodic action in preparations of low toxicity, and also weak anesthetic action.

#### EXPERIMENTAL

Succinate salt of 1-amino-2-methyl-2-benzylindan-3-one. To a suspension of 7.4 g of 1-imino-2-methyl-2-benzylindanone (VIa) hydrochloride [13] in 30 ml of glacial acetic acid was added 3.5 g of zinc powder. This was shaken and boiled 20 min, after which a second 3.5 g of zinc was added and it was boiled 20-25 min more. The clear solution was decanted from the unreacted zinc into 200 ml of water; 5 ml of concentrated hydrochloric acid was added and it was extracted several times with ether. The aqueous layer was made alkaline, extracted with ether, the ether extracts dried over anhydrous sodium sulfate, and evaporated to dryness. The residue was dissolved in a warm solution of 3 g of succinic acid in 15 ml of methanol, cooled, and 100 ml of ether was added. The succinate salt of the amine (2.34 g; 29%) precipitated during a day (it was possible to isolate a small quantity of a by-product, also the salt of a primary amine which was not accurately identified, from the filtrate). The colorless crystals, m.p.  $164-165^\circ$  (from water), were very soluble in alcohol and acetic acid.

Found %: N 3.95.  $C_{21}H_{23}O_5N$ . Calculated %: N 3.79.

1-Amino-2-methyl-2-benzylindan-3-one (VIIa). A suspension of the succinate salt in water was made alkaline and the amine was freed. The colorless needles (from a mixture of ether and petroleum ether) melted at  $75-76^\circ$  (sintered at  $65^\circ$ ). They were very soluble in most organic solvents. The amine salt of strong acids (VIIa) were difficult to separate in pure form, since they were extremely soluble in water and were hygroscopic.

Found %: N 5.91.  $C_{17}H_{17}ON$ . Calculated %: N 5.58.

Acetyl derivative of amine (VIIa). The succinate salt (1 g) of amine (VIIa) was boiled with 3.5 ml of acetic anhydride in 2.5 ml of acetic acid for 2 hr. Several ml of alcohol were added and it was boiled several min more and the solution poured into water. The white powder (0.63 g; 79%) melted at  $154-155^\circ$  (from dilute alcohol\*).

Found %: N 4.65.  $C_{19}H_{19}O_2N$ . Calculated %: N 4.78.

1-Amino-2-phenyl-2-benzylindan-3-one hydrochloride (VIb). To a suspension of 2.94 g of VIb in 10 ml of acetic acid was added 1.3 g of zinc powder, which was stirred thoroughly and boiled a half hour. A second 1.3 g of zinc was added and it was boiled another half hour. The solution was decanted from the unreacted zinc into 50 ml

\* Ratio of alcohol: water = 1 : 1 throughout.



of water and 30 ml of conc hydrochloric acid was added. The mixture was extracted twice with 40 ml of ether. The ether extract and water layer precipitated amine hydrochloride on standing. The total obtained was 0.96 g (32%). Colorless crystals, m.p. 164.5-165.5° (from dilute alcohol). The compound was somewhat different from its 2-methyl analog, which partly hydrolyzed in water, giving the free base (see below). It was soluble in water with difficulty.

Found %: N 4.04.  $C_{22}H_{20}ONCl$ . Calculated %: N 4.01.

1-Amino-2-phenyl-2-benzylindan-3-one (VIIb). Amine hydrochloride (VIIb, 0.2 g) was dissolved in dilute alcohol and made alkaline. The oil which separated crystallized on rubbing with a glass rod, after which water was added to the mixture to precipitate the amine completely. After several days 0.155 g (86%) of colorless crystals, m.p. 150.5-151.5° (from alcohol) separated.

Found %: N 4.50.  $C_{22}H_{19}ON$ . Calculated %: N 4.47.

1-Phthalimido-2-phenyl-2-benzylindan-3-one. Amine hydrochloride (0.3 g) was boiled in 5 ml of glacial acetic acid with 0.3 g of phthalic anhydride for 2.5 hr. The mixture was added to 50 ml of water, heated to boiling and diluted with water until the product became resinous (this method was repeated twice more). The phthalimide derivative was crystallized from alcohol. Colorless crystals, m.p. 206-207°.

Found %: N 3.28.  $C_{30}H_{24}O_3N$ . Calculated %: N 3.16.

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# STUDY OF POLYMERIZATION OF CYANO-CONTAINING ORGANOSILICON COMPOUNDS

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Within the past year studies of organosilicon compounds containing a CN group in the radical attached to the silicon atom have attracted attention. Polymers, obtained from these compounds, have a series of valuable properties [1]. Cyanoalkyl organosilicon polymers were initially used commercially as rubbers and rubber-like pastes [1,2]. One of us [3] previously synthesized a series of silicon-containing nitriles including  $\alpha$ -cyanoisopropoxyalkenylsilanes. The latter are characterized by their fair hydrolytic stability.

The present work was devoted to studying polymerization tendencies of cyano-containing alkenylsilanes.

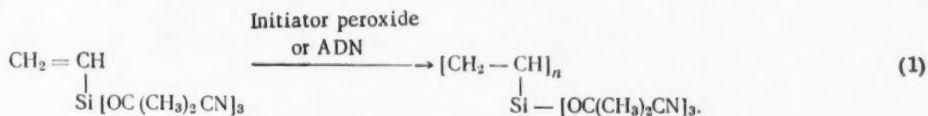
Polymerization was carried out both under pressure (6000 atm) in the presence of radical-type initiators and without excess pressure with platinum on carbon or chloroplatinic acid catalysts. The experimental results are given in Table 1.

The investigation showed that polymerization of cyanoisopropoxyalkenylsilanes must be conducted at relatively low temperatures; above 120° decomposition of these compounds is observed as in the case of their polymerization with peroxide initiators under pressure. A colorless polymer was obtained only in experiments in which isobutyric acid azodinitrile (ADN) was used as initiator at 80°. Yellow to brown-colored polymers were obtained in the remaining cases. Some experiments were terminated by polymerizate explosion with carbonization of the products.

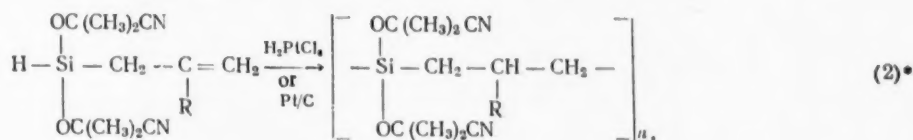
The majority of the polymers obtained, as is seen from Table 1, exhibited organic solubility.

We also conducted experiments for the reaction of tetraalkyldihydrodisiloxanes with diallyl cyano-containing silanes (23 and 24). Oily products, as from the earlier reaction of the same disiloxanes with dialkyldiallylsilanes [5], were thus obtained.

Conversion of the monomers presented in Table 1, in the cases when explosive polymerization with carbonization products did not occur, can be represented by the following scheme:



Apparently polymerization of dialkenyl cyano-containing compounds, possibly with formation of cyclic structures [6], also occurs at the double bonds, since some of the polymers we obtained were soluble.



\* As was shown previously for other compounds [4].

TABLE 1

Expt. No.	Monomer	Experimental conditions; pressure (atm); initiator (mole-%); temperature (°C)	Superficial appearance of polymerization product	Yield of pure polymer, wt.-%	Mol wt or reduced viscosity <sup>3</sup>	Solubility of polymer
1	$\text{CH}_2=\text{CH}-\text{Si}[\text{OC}(\text{CH}_3)_2\text{CN}]_2$	6000; ADN (0.5); 80	Colorless spongy resinous mass	20	810	In benzene
2	The same	The same; ADN (0.35) without initiator	The same	80	0.01** 0.02 polymerize	In dimethylformamide The same
3				60		
4				72		
5				not		
6	$\text{CH}_2=\text{CH}-\text{Si}[\text{OC}(\text{CH}_3)_2\text{CN}]_3$	6000; PB (0.35); 80 6000; PTB (1); 180 The same 150° 6000; PTB (1); 180	Did Colorless viscous oil Light brown gelatinous mass Gelatinous yellos mass Charred mass The same Black	32	656	In benzene In dimethylformamide The same
7				45		
8				48		
9						
10	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}[\text{OC}(\text{CH}_3)_2\text{CN}]_3$	The same 120° 6000; PTB (1); 180 The same 120° The same 6000; PTB (1); 150	Viscous yellow oil Charred mass Viscous oil Yellow transparent glass Dark-brown mass	44	544	Partly in dimethylformamide In benzene In dimethylformamide Insoluble In dimethylformamide
11				14		
12				Crosslinked		
13				30		
14	$\text{CH}_2=\text{CH}-\text{CH}_2\text{O}-\text{Si}[\text{OC}(\text{CH}_3)_2\text{CN}]$			~ 100		Partly in dimethylformamide
15	$(\text{CH}_2=\text{CH}-\text{CH}_2\text{O})_2\text{SiOC}(\text{CH}_3)_2\text{CN}$	The same	Black			In dimethylformamide
16	$(\text{CH}_2=\text{CH}-\text{CH}_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{CN}$	6000; PTB (1); 120	Red-brown solid	25	0.04	In dimethylformamide

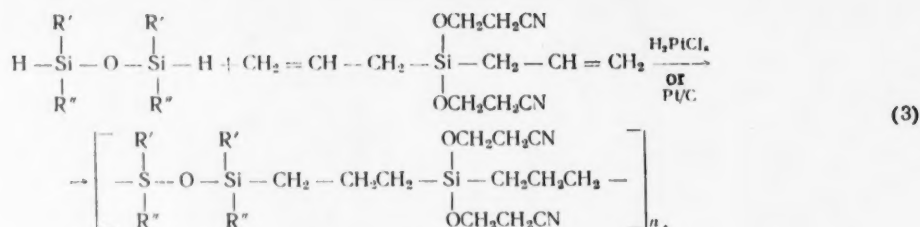
TABLE 1 (Continuation)

Expt. No.	Monomer	Experimental conditions; pressure (atm); initiator (mole-%); temperature (°C)	Superficial appearance of polymerization product	Yield of pure polymer, wt %	Mol wt or reduced viscosity***	Solubility of polymer
17	$\text{CH}_2=\text{CH}-\text{Si}-(\text{OCH}_2\text{CH}_2\text{CN})_2$	6000; PB (0.37); 80	Yellow oil	30		In benzene
18	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}-[\text{OC}(\text{CH}_3)_2\text{CN}]_2$	1.5% platinum on carbon (1.1 g on 1 mole); 180	Dark-brown mass	67		Insoluble in dimethylformamide
19	The same	1; 0.1 M solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in isopropyl alcohol (0.005 g); 120	Viscous oil	75	1070	In benzene
20	"	6000; PB (0.37); 80	Dark-yellow	35	0.05	In dimethylformamide
21	$\text{CH}_2=\text{C}-\text{CH}_2-\text{Si}-[\text{OC}(\text{CH}_3)_2\text{CN}]_2$	1; 5% platinum on carbon (1.1 g on 1 mole); 150	Viscous yellow oil	73	1320	In benzene
22	The same	The same 180°	Dark-brown mass	70		Insoluble in dimethylformamide
23	$(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{Si}-[\text{OC}(\text{CH}_3)_2\text{CN}]_2$ + $\text{H}-\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)-\text{O}-\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)-\text{H}$	1; 0.1 M solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in isopropyl alcohol (0.005 g); 120°	Mobile oil	71	1018	In benzene
24	$(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{Si}(\text{OCH}_2\text{CH}_2\text{CN})_2$ + $\text{H}-\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)-\text{O}-\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)-\text{H}$	The same	Yellow oil	62	1130	In benzene

\* Length of experiment 6 hr; ADN is isobutyric acid azodinitrile; PTB is tert-butyl peroxide; PB is benzoyl peroxide.

\*\* Reduced viscosity  $\eta_{\text{red}}/C$  in dimethylformamide at 20°;  $C = 0.4\%$

\*\*\* Mol wt was determined cryoscopically in benzene.



## EXPERIMENTAL

The preparation of monomers, other than the three for which synthesis and properties are presented below, was described previously [7, 8].

Diallyldi-( $\beta$ -cyanoethoxy) silane was obtained by method [1] from 0.25 g-mole of diallyldichlorosilane, 0.5 g-mole of  $\beta$ -cyanoethyl allyl ether, and 0.6 g-mole of pyridine in 100 ml of dry benzene. The crude yield of product boiling at 178-181°/10 mm (little decomposition) was about 40%. After a second distillation the material had the following constants:

$n_D^{20}$  1.4674;  $d_4^{20}$  1.0283;  $MR_D$  found 67.60; calculated 67.98.  
 Found %: C 56.95; 56.99; H 7.83; 7.63; Si 10.03; 9.88  $C_{12}H_{18}SiO_2N_2$ .  
 Calculated %: C 57.56; H 7.24; Si 11.20.

Vinylmethyldi-( $\beta$ -cyanoethoxy)-silane was obtained by an analogous procedure with the corresponding reagents with a b.p. of 165-175°/13 mm in 76 M yield; after a second distillation it boiled at 178°/18 mm;

$n_D^{20}$  1.4475;  $d_4^{20}$  1.0428;  $MR_D$  found 53.94; calculated 54.25.  
 Found %: Si 13.20; 13.60  $C_9H_{14}SiO_2N_2$ . Calculated %: Si 13.30.

Vinylmethyldi-( $\alpha$ -cyanoisopropoxy)-silane was obtained similarly from the corresponding reagents in 47% yield; b. p. 120-175°/5 mm. After a second distillation the b.p. was 123-124°/5 mm;

$n_D^{20}$  1.4298;  $n_D^{20}$  0.9729;  $MR_D$  found 63.22; calculated 63.30.  
 Found %: Si 12.0; 12.1  $C_{11}H_{16}SiO_2N_2$ . Calculated %: Si 11.8.

Polymerization. Polymerization under pressure was carried out in lead ampoules. The experimental technique was described in preceding articles [9]. Experiments without excess pressure in the presence of platinum on carbon or chloroplatinic acid catalysts were conducted in sealed glass ampoules. The polymers were purified by distilling the unreacted monomer in the case of oily products or by reprecipitation from dimethylformamide. Insoluble polymers were purified by repeated treatment with benzene or dimethylformamide.

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# THE STRUCTURE OF "ANOMALOUS" AMINONITRILE COMPLEX COMPOUNDS OF DIVALENT PLATINUM

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Until recently only one opinion was held about the structure of "anomalous" aminonitrile complex compounds of divalent platinum: this was first disclosed by L. A. Chugaev and V. V. Lebedinskii [1] and had the composition  $[\text{Pt}(\text{RCN})_2\text{A}_4]\text{X}_2$  or  $[\text{PtRCNA}_4]\text{X}_2$  where RCN is a nitrile, A an amine, and X a univalent anion. Divalent platinum in these compounds has a formally anomalously high coordination number of 6 or 5, from which these compounds obtained the designation "anomalous." V. V. Lebedinskii and V. A. Golovnya [2] came to the conclusion, as a result of their study on reactions of the "anomalous" compounds, that the "spare" (above the 4 coordination number for divalent platinum) amines are bound not to the platinum but to the nitrile so the coordination number of divalent platinum is indeed equal to 4. Amplifying this view point, A. A. Grinberg and Kh. I. Gil'dengershel' [3] postulated that amidines were formed by the reaction of "spare" amines with nitriles. However, Harris and Stephenson [4] interpreted the x-ray data they obtained for  $[\text{Pt}(\text{CH}_3\text{CN})_2(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$  using a complex cation structure in which divalent platinum has a coordination number of 6, but 4 ammonia molecules and 2 acetonitrile molecules exhibit octahedral coordination in which both acetonitrile molecules are found trans to each other and are bound to platinum through the  $\text{C} \equiv \text{N}$  triple bond.

In order to clarify the structure of "anomalous" compounds we studied the IR absorption spectra ( $400\text{--}4000\text{ cm}^{-1}$ ) of nitrile compounds of the type  $[\text{Pt}^{\text{II}}(\text{RCN})_2\text{X}_2]$  (where  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) and  $\text{cis-}[\text{Pt}^{\text{IV}}(\text{RCN})_2\text{Cl}_4]$ , anomalous compounds

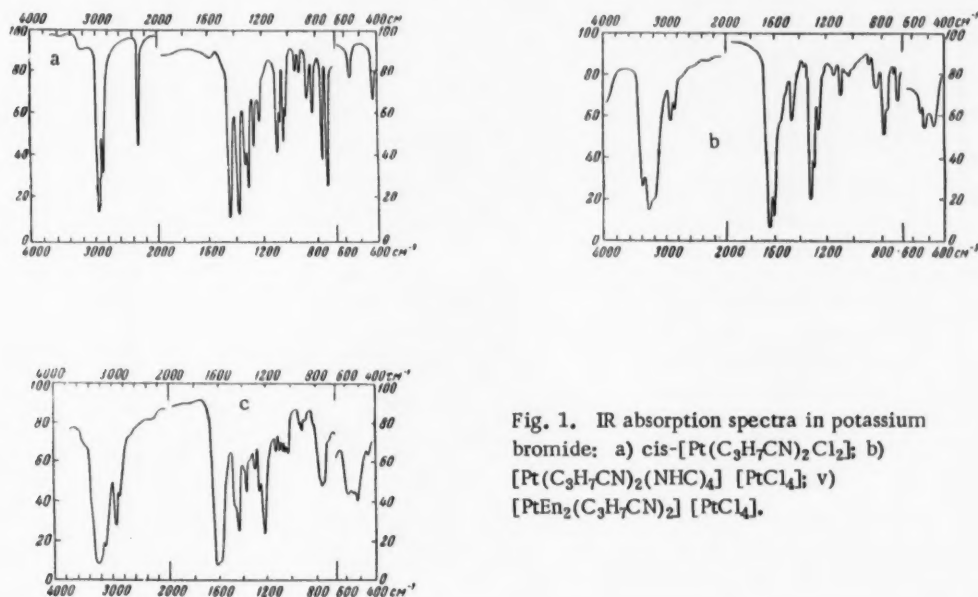


Fig. 1. IR absorption spectra in potassium bromide: a)  $\text{cis-}[\text{Pt}(\text{C}_3\text{H}_7\text{CN})_2\text{Cl}_2]$ ; b)  $[\text{Pt}(\text{C}_3\text{H}_7\text{CN})_2(\text{NHC}_4\text{H}_9)_4][\text{PtCl}_4]$ ; c)  $[\text{PtEn}_2(\text{C}_3\text{H}_7\text{CN})_2][\text{PtCl}_4]$ .

(as chloroplatinic derivatives) with ammonia, methyl and ethyl amines, and some complexes containing the same ligands but not being "anomalous."\* The compounds were studied in the solid state. Potassium bromide pellets and vaseline oil mulls were the methods used.

In spectra for the compounds  $[\text{Pt}(\text{RCN})_2\text{X}_2]$  and  $\text{cis-}[\text{Pt}(\text{RCN})_2\text{Cl}_4]$  the triple bond  $\text{C} \equiv \text{N}$  valence vibration appeared in the region  $\sim 2300 \text{ cm}^{-1}$  (Table 1). This frequency increased 50–70  $\text{cm}^{-1}$  in comparison with the frequency for free liquid nitriles [5]. A typical spectrum is given in Fig. 1. Increasing  $\nu (\text{C} \equiv \text{N})$  is evidence for coordination of the nitrile not through the  $\text{C} \equiv \text{N}$  triple bond but at the expense of the unshared electron pair of the nitrogen atom, since by coordination through the triple bond one would expect a decrease in  $\nu (\text{C} \equiv \text{N})$  owing to some weakening of the  $\text{C} \equiv \text{N}$  bond by withdrawing the electron cloud from this bond toward the platinum atom. This frequency lowering is observed in coordination of molecules through multiple bonds  $\text{C} = \text{C}$  [6], and  $>\text{C} = \text{C}<$  [7, 9]. Considering an analogous increase in  $\nu (\text{C} \equiv \text{N})$  during formation of the  $\text{R}-\text{C} \equiv \text{N} \rightarrow \text{M}$  bond, where M is the complex-forming atom, in other nitrile complexes [10–13] we suggested the possible outcome that withdrawing the unpaired electron pair from the nitrogen atom of the nitrile would lead to some strengthening of the  $\text{C} \equiv \text{N}$  bond, i.e., the unshared electron pair on the nitrogen atom exerts a weakening effect on the  $\text{C} \equiv \text{N}$  bond.

TABLE 1. Wave Numbers of Absorption Peak Maxima,  $\text{cm}^{-1}$  (p-discontinuity)

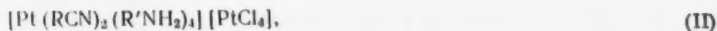
		$\nu (\text{NH})$	$\nu (\text{C} \equiv \text{N})$	$\nu (\text{C} = \text{N})$
as	$[\text{Pt}(\text{CH}_3\text{CN})_2\text{Cl}_2]$	—	2300, 2314 p	—
as	$[\text{Pt}(\text{CH}_3\text{CN})_2\text{Br}_2]$	—	2314	—
trans	$[\text{Pt}(\text{CH}_3\text{CN})_2\text{Cl}_2]$	—	2307	—
as	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{Cl}_2]$	—	2303	—
as	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{Br}_2]$	—	2305	—
as	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{Cl}_2]$	—	2311	—
as	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{Br}_2]$	—	2305	—
as	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{Cl}_2]$	—	2305	—
as	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{Cl}_2]$	—	2280	—
	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{Cl}_2]$	—	2319	—
	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{Cl}_2]$	—	2312	—
	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{Cl}_2]$	—	2319	—
	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{Cl}_2]$	—	2288	—
	$[\text{Pt}(\text{CH}_3\text{CN})_2(\text{NH}_3)_2][\text{PtCl}_4]$	~3170 n, ~3290, 3412	—	1638
	$[\text{Pt}(\text{CH}_3\text{CN})_2(\text{NH}_3)_2][\text{PtCl}_4]$	~3237 n, ~3300, 3409	—	1635
	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2(\text{NH}_3)_2][\text{PtCl}_4]$	Some bands at ~3230–3430	—	1640
	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2(\text{NH}_3)_2][\text{PtCl}_4]$	3140–3240	—	1629
as	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{NH}_2\text{Cl}_2]$	31172, 3241, 3289	2302	—
	$[\text{Pt}(\text{CH}_3\text{CN})_2\text{En}_2][\text{PtCl}_4] \cdot \text{H}_2\text{O}$	~3175, ~3440	—	1617
	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{En}_2][\text{PtCl}_4] \cdot \text{H}_2\text{O}$	3126, 3236, ~3450	—	1607
	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{En}_2][\text{PtCl}_4]$	3126, ~3238, ~3470 n	—	1602
	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2\text{En}_2][\text{PtCl}_4]$	3126, ~3241, ~3430 n	—	1605
	$[\text{Pt}(\text{CH}_3\text{CN})_2\text{En}_2][\text{PtCl}_4]$	~3120, 3213, 3279, ~3470	—	1623
	$[\text{PtEn}_2]\text{Cl}_2$	3063, 3146	—	—
	$[\text{Pt}(\text{CH}_3\text{CN})_2(\text{CH}_3\text{NH}_2)_2][\text{PtCl}_4]$	3136, 3221, 3298, 3354	—	1617
	$[\text{Pt}(\text{C}_2\text{H}_5\text{CN})_2(\text{CH}_3\text{NH}_2)_2][\text{PtCl}_4]$	3131, ~3220, 3287, ~3460 n	—	1623
as	$[\text{Pt}(\text{CH}_3\text{NH}_2)_2\text{Cl}_2]$	3129, 3226, 3271	—	—

\* Similar spectral descriptions will be presented later.

While deciding the question whether the "anomalous" complexes contained amidines and amines, i.e. the following formula



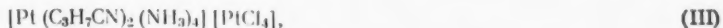
or nitriles and amines, i.e., this formula



where  $\text{R}' = \text{H}$  or a hydrocarbon radical, we started with the fact that spectra of the complexes, as a function of structure I or II, must exhibit the following features. In the spectra of compound I the absorption bands at  $3300\text{--}3500\text{ cm}^{-1}$  ( $\nu(\text{NH})$  for a non-coordinated group  $-\text{NH}_2$  or  $=\text{NH}$  [14,15]) and at  $1600\text{ cm}^{-1}$  ( $\nu(\text{C}=\text{N})$  [14]) must be present, but in compound II they must be absent. On the contrary, the absorption band relating to  $\nu(\text{C}\equiv\text{N})$  of coordinated nitriles must be absent in spectra of compound I but present in spectra of compound II. In the spectra we obtained of "anomalous" complexes (typical spectra are given in Fig. 1, b, v) the absorption peak which must be due to  $\nu(\text{C}\equiv\text{N})$  is absent. There is an absorption peak in the  $\sim 3400\text{ cm}^{-1}$  region, which must refer to  $\nu(\text{NH})$  or non-coordinated  $\text{NH}$  or  $\text{NH}_2$  groups, since the absorption band for coordinated groups commonly lies in the region  $< 3300\text{ cm}^{-1}$ . There is an intense doublet at about  $1600\text{ cm}^{-1}$  in the spectra of all the "anomalous" compounds, the higher frequency component of which changes its position and intensity only slightly on deuteration of the  $\text{N-H}$  bond and therefore must be due to the  $\nu(\text{C}=\text{N})$ . In complete agreement with this behavior the value of  $\nu(\text{C}=\text{N})$  for deuterated "anomalous" butyronitrile complexes with ammonia ( $1613\text{--}1615\text{ cm}^{-1}$ ) is between the value of  $1640\text{ cm}^{-1}$  found for the  $>\text{C}=\text{N-H}$  group and the calculated value of  $1592\text{ cm}^{-1}$  calculated for the hypothetical  $>\text{C}=(\text{ND})$  group. The lower-frequency component of the doublet disappeared on deuteration and consequently must be due to the  $\text{N-H}$  deformation frequency.

Thus it was possible to demonstrate that the "anomalous" compounds actually contain amidines and correspond to formula I. The presence of the intense doublet in the  $\sim 1600\text{ cm}^{-1}$  region is a further characteristic indication of unsubstituted  $\text{N-alkylmonosubstituted}$  amidines in the complexes.

Although we found the first proof that the amidine group ( $=\text{NH}$  or  $-\text{NHR}'$ ) is bound to platinum, a series of arguments is evidence for coordination through the  $=\text{NH}$  group. It is known [14, 15] that the absorption band assigned to  $\nu(\text{NH})$  in the non-coordinating  $\text{C}=\text{NH}$  group lies in the  $3200\text{--}3400\text{ cm}^{-1}$  region. In the spectra of "anomalous" compounds with En of the type  $[\text{PtEnRC}(=\text{NH})\text{NH}(\text{CH}_2)_2\text{NHC}(=\text{NH})\text{R}][\text{PtCl}_4]$  the frequency for the non-coordinating  $\nu(\text{NH})$  group is identified at  $3430\text{--}3470\text{ cm}^{-1}$ , i.e. in the region  $> 3400\text{ cm}^{-1}$ . Consequently they, obviously, can not be assigned to  $\nu(\text{NH})$  of the non-coordinated  $\text{C}=\text{NH}$  group. In other words, the  $\text{C}=\text{NH}$  group apparently is not free, but is bound to platinum. Further, using the Bellamy - Williams equation [16] for the frequencies of symmetrical and asymmetrical valence vibrations of non-coordinated amine groups  $\nu_s = 345.5 + 0.876$  it is possible to show that in the "anomalous" complexes with ammonia, evidently, the amino group is not coordinated. In the spectrum of



partial deuteration to decrease the band intensity assigned to  $\nu(\text{NH})$  identified the  $\nu(\text{NH})$  frequencies as equal to  $3429, 3395, 3359$ , and  $3310$ , which can be assigned to non-coordinated  $\text{NH}_2$  or  $\text{NH}$  groups ( $> 3300\text{ cm}^{-1}$ ). If the first two bands are assigned to  $\nu_{\text{as}}(\text{NH}_2)$  (the appearance of two peaks must indicate the presence of two groups or resonance splitting), then the values of  $\nu_s(\text{NH}_2)$  calculated by the Bellamy-Williams relationship are equal to  $3349$  and  $3320\text{ cm}^{-1}$ , which agree well with the found values of  $3359$  and  $3310\text{ cm}^{-1}$ . The increasing difference  $\pm 10\text{ cm}^{-1}$  between the calculated and found values in comparison with the common ones ( $4.8\text{ cm}^{-1}$  for solutions of amines) is not unexpected since our measurement errors in this region can be  $\pm 4\text{--}5\text{ cm}^{-1}$ . Moreover, a considerable divergence from the Bellamy-Williams relationship for solid substances owing to their large intermolecular interaction is not excluded. Thus the feasibility of the Bellamy-Williams equation for complex III is evidence that there is a non-coordinated amine group in III, i.e. coordination occurs through the  $=\text{NH}$  group.

We think that amidine formation does not occur by cleavage of the platinum-nitrile nitrogen bond as proposed in [17], but that the amine reacts with the nitrile within the complex. This supposition is consistent with coordination of amidines through the  $=\text{N-H}$  group and formation of cis complexes. The cis configuration of the complexes was previously demonstrated by acidic cleavage of "anomalous" aminonitrile compounds.

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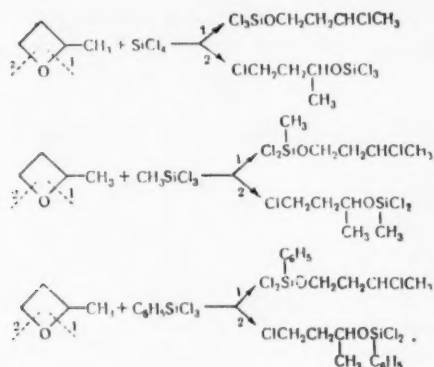
THE REACTION OF  $\alpha$ -METHYLTRIMETHYLENE OXIDE  
WITH CHLOROSILANES, ALUMINUM CHLORIDE,  
AND TITANIUM TETRACHLORIDE

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Original article submitted July 13, 1961

Trimethylene oxide, as well as other organic oxides, reacts with various halogen-containing agents. Hydrogen bromide and phosphorus pentachloride cleave trimethylene oxide with elimination of an oxygen atom and formation of the corresponding 1,3-dibromo and 1,3-dichloropropanes. Acetyl chloride, on reaction with trimethylene oxide forms  $\gamma$ -chloropropyl acetate [1]. Searles and his associates [2] studied the reaction between  $\alpha$ -methyltrimethylene oxide and hydrogen halides (HCl, HBr) and acetyl chloride and showed that cleavage of the  $\beta$ -oxide occurred mainly at the C-O-bond not connected to the methyl group.

In this work we studied the reaction between  $\alpha$ -methyltrimethylene oxide and some chlorosilanes ( $\text{SiCl}_4$ ,  $\text{CH}_3\text{SiCl}_3$ , and  $\text{C}_6\text{H}_5\text{SiCl}_3$ ), aluminum chloride, titanium tetrachloride, and hydrogen chloride. The primary goal of our study was to determine the direction in which a  $\beta$ -oxide ring, containing an alkyl group in the  $\alpha$ -position, would cleave on treatment with different halogen-containing agents. Silicon tetrachloride, methyltrichlorosilane, and phenyltrichlorosilane reacted energetically with  $\alpha$ -methyltrimethylene oxide even at room temperature in the absence of a catalyst. By distilling the reaction products under reduced pressure the chlorosubstituted esters of orthosilicic acid were isolated. The nature of the products obtained showed that the reaction occurred according to the following scheme:



The orthosilicic esters were subjected to hydrolysis as a result of which chlorohydrins were obtained.

The reaction between  $\alpha$ -methyltrimethylene oxide and HCl was conducted by passing dry hydrogen chloride through a solution of the pure oxide at its boiling point. At the end of the reaction the temperature of the reaction mixture was increased to 105-110° by the reaction heat.

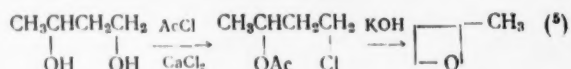
Aluminum chloride and titanium tetrachloride reacted with  $\alpha$ -methyltrimethylene oxide so energetically that the reaction between them occurred satisfactorily only on cooling to -50, -60°. The reaction products were subjected to hydrolysis with water in ethereal medium with cooling. Alcohols containing a primary or secondary chlorine atom were obtained as a result of hydrolysis. In all cases a very strong absorption band around 660 wave num-



bers ( $\text{cm}^{-1}$ ), characteristic of a primary chlorine atom [3], was observed in the diffuse-light spectra of these chlorohydrins. An absorption band at about  $610 \text{ cm}^{-1}$  (wave numbers), characteristic of a secondary halide, was also observed in the spectra, but was much less intense. This means that the chlorohydrin mixture is primarily 4-chlorobutanol-2. This result leads to the following conclusion:  $\alpha$ -methyltrimethylene oxide on reaction with various halogen-containing agents is cleaved mainly at the ether bond not connected to the methyl group. For comparison, in the case of asymmetric  $\gamma$ -oxides, for example tetrahydrosilvane [4], ring cleavage by chlorosilanes occurs at the C-O bond connected to the methyl group.

## EXPERIMENTAL

$\alpha$ -Methyltrimethylene oxide was obtained by the following scheme:



Cyclization of 1-chloro-3-acetoxybutane to  $\alpha$ -methyltrimethylene oxide was accomplished by heating the chloroacetate to  $160\text{--}170^\circ$  with potassium hydroxide; the  $\beta$ -oxide being formed was not distilled from the reaction zone. After distillation through a column it had the following constants: b.p.  $60^\circ$  (759 mm),  $n_D^{20}$  1.3900;  $d_4^{20}$  0.8557. Found  $\text{MR}_D$  19.97;  $\text{C}_5\text{H}_{10}\text{O}$ . Calculated  $\text{MR}_D$  20.11.

The chlorosilanes used were distilled through a column and boiled at  $58\text{--}60^\circ$  (silicon tetrachloride),  $64\text{--}65^\circ$  (methyltrichlorosilane), and  $199\text{--}201^\circ$  (phenyltrichlorosilane).

The reaction between silicon tetrachloride, methyltrichlorosilane, or phenyltrichlorosilane and  $\alpha$ -methyltrimethylene oxide was conducted in the following manner.

$\alpha$ -Methyltrimethylene oxide (1 g-mole) was added slowly at room temperature to the halosilane taken in two-fold excess. The reaction occurred with marked heat evolution. After adding all the  $\beta$ -oxide the reaction mixture was heated to boiling for 5-6 hr. The orthosilic acid esters obtained in about 80% yields were separated from the reaction products by distillation under reduced pressure. The properties of these esters are given in Table 1. The orthosilic chloroesters were then subjected to hydrolysis with water. The two chlorohydrins obtained as a result of this indicate the formation of two orthosilic esters.

A fraction boiling at  $42\text{--}45^\circ$  (5 mm) with  $n_D^{20}$  1.4433, which consisted of a mixture of chlorobutanols, was isolated by distillation of the hydrolysis products. The following data are given in the literature for the isomeric chlorobutanols we obtained: 4-chlorobutanol-2, b.p.  $67^\circ$  (20 mm),  $n_D^{20}$  1.4408 [5]; 3-chlorobutanol-1, b.p.  $66\text{--}68^\circ$  (15 mm),  $n_D^{27}$  1.4396 [6].

TABLE 1. Properties of Chloro-substituted Orthosilic Esters

Empirical formula for orthosilic chloroester	B.p., $^\circ\text{C}$ (mm)	$n_D^{20}$	Found, %				Calculated, %			
			C	H	Cl	Si	C	H	Cl	Si
$\text{C}_4\text{H}_9\text{SiOC}_4\text{H}_9\text{Cl}$	$56^\circ$ (5)	1.4403	20,36	3,33	58,21	11,40	19,85	3,30	58,60	11,54
$\text{CH}_3\text{SiCl}_2\text{OC}_4\text{H}_9\text{Cl}$	$39\text{--}42$ (5)	1.4375	27,90	5,20	47,07	12,23	27,10	5,00	48,00	12,66
$\text{C}_4\text{H}_9\text{SiCl}_2\text{OC}_4\text{H}_9\text{Cl}$	$132\text{--}136$ (8)	1.5082	42,28	4,91	37,31	9,86	42,28	4,62	37,50	9,89

The chlorobutanols were subjected to acetylation with acetic anhydride. The chlorohydrin and acetic anhydride, taken in two-fold excess, were mixed in an Erlenmeyer flask for this purpose. The mixture was left for 5 hr with ice cooling and then at room temperature for one day. After distilling the unreacted acetic anhydride the acetylation products were distilled under reduced pressure. The fraction containing  $\gamma$ -chlorobutyl acetate boiled at  $38\text{--}41^\circ$  (6 mm) and had  $n_D^{20}$  1.4260. The reaction between  $\alpha$ -methyltrimethylene oxide and dry hydrogen chloride was carried out in the following manner: 1 g-mole of the  $\beta$ -oxide was placed in a flask and hydrogen chloride was passed through it at the boiling point of the  $\beta$ -oxide. The reaction usually was complete when the temperature of the reaction mixture reached  $102^\circ$ . This was then washed with a 5% soda solution, then with water, dried over mag-

nesium sulfate, and distilled under reduced pressure. The mixture of chlorobutanols obtained was analyzed by the combination diffuse-light method. Aluminum chloride was added in portions of approximately 1 g, while titanium tetrachloride was added from a dropping funnel in small portions to carefully stirred  $\alpha$ -methyltrimethylene oxide cooled to  $-50, -60^\circ$ . Ether was added to the reaction mixture at the end of the reaction and then hydrolysis with water was carried out with cooling. The chlorobutanols were extracted from the water layer with ether. The ether extracts were washed with soda solution, then with water, and dried with potassium carbonate; after distilling the ether the chlorobutanols were distilled under vacuum.

The combination disperse-light spectra were taken by G. K. Gaivoronskii, whom the authors thank.

The reactions of  $\alpha$ -methyltrimethylene oxide with chlorosilanes, aluminum chloride, titanium tetrachloride, and hydrogen chloride were studied. In all cases cleavage of the  $\beta$ -oxide ring occurs in both possible ways, but preferentially at the ether bond not connected to the methyl group. The orthosilicic esters formed as a result of the reaction between  $\alpha$ -methyltrimethylene oxide and chlorosilanes are substitution products of  $\gamma$ -chlorobutoxysilyl groups for one chlorine atom in the molecule of the starting chlorosilane.

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# MASS SPECTROMETRIC STUDY OF THE VAPOR COMPOSITION ABOVE RARE EARTH OXIDES

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(Presented by Academician A. N. Terenin, June 26, 1961)

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Original article submitted June 23, 1961

Chupka, et. al. [1] studied the composition of vapor in equilibrium with lanthanum oxide at high temperatures by mass-spectrometric methods and found that only lanthanum monoxide and atomic oxygen are present in the vapors; it was also shown that the saturated vapor pressure at 1860° K was  $2.2 \cdot 10^{-7}$  atm. White, Goldstein, and Walsh [2] studied the vapor pressure of lanthanum and neodymium monoxides over the corresponding trioxides in the temperature range 2230-2440° K by effusion methods. Comparing data on the energetics of forming condensed oxides with the enthalpy of sublimation of metals and considering the scarcity of values for the dissociation energy of gaseous monoxides, the authors concluded that the stability of gaseous molecules MO must be lower with increasing periodic number of the starting element. Ackermann and Thorn [3], in their review, examined the results of work [1, 2] which confirms that the value for the vapor pressure of LaO measured by Chupka et. al. is too high. Panish [4] communicated the results of a mass-spectrometric study of vapor composition over neodymium, praseodymium, samarium, and europium oxides paying great attention to avoiding reaction of materials being studied with the material in the container, on which iridium or thorium oxide was deposited for this purpose. They discovered changes in the main gaseous products in going through the series from PrO to Eu; gaseous  $\text{PrO}_2$  was also found over praseodymium oxide in small amounts.

We studied the vapor composition over all the rare-earth oxides except thulium. The study was conducted on the MI-1305 mass spectrometer. The scheme for ion generation is given in Fig. 1. The substance being studied was

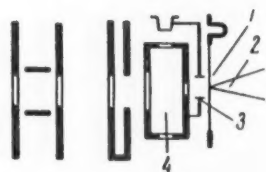


Fig. 1. Scheme for ion generation.

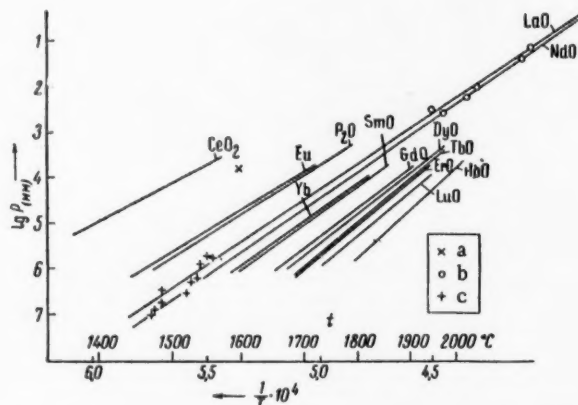


Fig. 2. Vapor pressure over the oxides of rare-earth elements. a) Data from Inghram et. al. [1]; b) data from White et. al. [2]; v) our data.

deposited in a thin layer on the central part of the iridium band-evaporator (1) to which was welded a thermocouple (2) prepared from tungsten-rhenium alloys containing 5 and 20% of rhenium, respectively [5]. The thermocouple was calibrated with a first-class optical pyrometer in the Mendelev High Temperature Laboratory of the All-Union Scientific Institute. The deflecting plates (3) prevented hitting in the box for ionizing ions (4), which can be formed

at the ionization surface of the oxides studied. The construction of the source permitted operating the band-evaporator at temperatures to 2100°.

In interpreting results of mass-spectrometric studies with the goal of obtaining quantitative data on the corresponding partial pressure of the component gases, particular attention must be paid to the possibility of simultaneous formation of ions with equal masses by direct ionization of neutral molecules and, moreover, by dissociative ionization of much heavier molecules. Panish [4] considered that the ratio of ionic currents in mass spectra studied at an ionizing voltage of 20 v corresponded to the relative concentration of the corresponding neutral molecules in the vapors. This supposition seemed unfounded to us, since by arbitrary choice electronic energy, on one hand, can go into dissociative ionization to a considerable extent; on the other hand, effective ionization of isolated molecules, mainly of the type  $\text{MO}_2$ , can also be very small. We estimated a potential for the appearance of ions for all cases studied; the scale of ionizing voltage was corrected to a known ionization potential for argon and mercury. Then we extrapolated the initial section of the ionization curve from the time of initial ion-fragment formation to the maximum ionic current, when the value of the current had little dependence on the electronic energy. The ratio of ionic current at maximum effective ionization, with correction for the ratio of effective cross-section of ionization [6], nearly always corresponded to the concentration ratio of neutral molecules in the vapors over the given oxide.

The results of our study of vapor composition over oxides of the rare-earth elements are given in Table 1; mass-spectrometric data of vapors obtained at an ionizing current of 45 and 10 v are included in it; the largest ion current is taken as the unit in each of the cases. Measurements were taken at temperatures which allowed attaining a vapor pressure for the oxide component of about  $10^{-5}$  mm Hg for the different oxides. Using the previously described variant of Langmuir's [7] method we determined the vapor pressure of the gaseous monoxides over lanthanum and neodymium oxides. For the remaining oxides vapor pressure was estimated by simultaneous vaporization of equimolar amounts of the oxide being studied and lanthanum oxide. On Fig. 2 are given data for the vapor pressure of rare-earth monoxides, obtained both by us and by other investigators [1, 2, 4]. The pressure of the metal vapors was determined over europium and ytterbium oxides.

Examination of the experimental materials showed that the volatility of rare-earth under high vacuum as well as the composition of their vapors differs markedly for oxides of the various elements. The general tendency in the

TABLE 1. Mass Spectra of Vapors over Rare-earth Oxides

Oxide	Ionizing voltage					
	45 v			10 v		
	$\text{M}^+$	$\text{MO}^+$	$\text{MO}_2^+$	$\text{M}^+$	$\text{MO}^+$	$\text{MO}_2^+$
$\text{La}_2\text{O}_3$	0,16	1,0	—	—	1,0	—
$\text{CeO}_2$	0,28	0,6	1,0	—	1,0	0,95
$\text{Ce}_2\text{O}_3$	0,18	0,91	1,0	—	1,0	0,3
$\text{Pr}_2\text{O}_3$	0,36	1,0	0,2	—	1,0	0,01
$\text{Nd}_2\text{O}_3$	0,25	1,0	—	—	1,0	—
$\text{Sm}_2\text{O}_3$	1,0	0,99	—	1,0	0,77	—
$\text{Eu}_2\text{O}_3$	1,0	0,2	—	1,0	0,15	—
$\text{Gd}_2\text{O}_3$	0,3	1,0	—	1,0	0,83	—
$\text{Tb}_2\text{O}_3$	0,2	1,0	0,01	0,9	1,0	—
$\text{Dy}_2\text{O}_3$	0,5	1,0	—	1,0	0,59	—
$\text{Ho}_2\text{O}_3$	1,0	0,77	—	1,0	0,45	—
$\text{Er}_2\text{O}_3$	1,0	1,0	—	1,0	0,72	—
$\text{Yb}_2\text{O}_3$	1,0	0,01	—	1,0	—	—
$\text{Lu}_2\text{O}_3$	1,0	0,9	—	1,0	0,60	—

lanthanide series is a decrease in the stability of gaseous monoxides in going across the series from La to Lu compounds as a consequence of which the ratio  $\text{M}^+/\text{MO}^+$  increases. This regularity indicates distinct periodicity; the ratio  $\text{M}^+/\text{MO}^+$  is larger for oxides of those elements which exhibit a +2 valence (Eu, Yb) and have the minimum enthalpies for sublimation of the metal; these oxides also have higher volatility. In vapors above oxides of elements which exhibit +4 valence, we detected molecules of gaseous dioxides ( $\text{CeO}_2$ ,  $\text{PrO}_2$ ,  $\text{TbO}_2$ ). In control experiments we obtained analogous results vaporizing  $\text{Tb}_2\text{O}_3$  with tungsten strip, since the ionic current for  $\text{Ir}^+$  and  $\text{TbO}_2^+$  were not separated by our mass-spectrometer. Cerium dioxide, on heating under vacuum, dissociated to a composition near  $\text{CeO}_{1,80}$  —  $\text{CeO}_{1,67}$  [8]. This oxide, vaporizing, gives CeO and  $\text{CeO}_2$  molecules in its vapors. The ratio between  $\text{CeO}^+/\text{CeO}_2^+$  in the ionic current does not remain constant, but gradually increases as the amount of material on vaporizer decreases from 0,5 : 1,0 at the beginning of the experiment to 0,8 : 1,0 at the end (ionizing current of 45 v). The mass spectra of cerium oxide vapors also contains the  $\text{CeO}^+$  and  $\text{CeO}_2^+$  ions, the ratio of which ionic currents under our experimental conditions (residual pressure in mass

spectrometer at the experimental temperature is about  $6-8 \cdot 10^{-7}$  mm Hg) is about 0,95 : 1,0 and does not change as the sample is vaporized. Thus,  $\text{Ce}_2\text{O}_3$  is vaporized in proportion to the solid phase composition, close to  $\text{CeO}_{1,6}$ . Formation of ions of the type  $\text{M}_2\text{O}_3^+$  or polymeric ions  $(\text{MO})_n$  is not observed in any of these cases.

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# INFLUENCE OF TERMINAL SUBSTITUENTS IN 5-NITROFURYL POLYENE DERIVATIVES ON THEIR ELECTRONIC SPECTRA

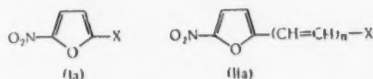
Ya. A. Eidus, K. K. Venter, and Academician Acad. Sci.  
Latv. SSR S. A. Giller

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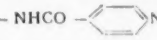

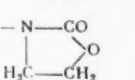
Original article submitted July 12, 1961

The question of the influence of different electron-accepting and electron-releasing substituents in 5-nitro-furan derivatives of type Ia on the shift of absorption maxima in the electronic spectra of these compounds has been considered in previous communications [1-3].



Recent work is devoted to development of rules for transferring the effects of terminal substituents X on the light absorption of 5-nitrofuran derivatives, if this influence is transferred from the main chromophore through the chain of conjugated bonds consisting of one to four  $-\text{CH}=\text{CH}-$  groups. We studied compounds having structure IIa ( $n = 0-4$ ) enumerated in Table 1.

TABLE 1. Derivatives of 5-Nitrofuryl Polyenes

No.	Terminal substituent X	$a_1$	$a_2$	$h_1$	$h_2$
I	$\text{X} = -\text{COOC}_2\text{H}_5$	8,7	4,0	2,4	1,6
II	$\text{X} = -\text{CO}-\text{CH}_3$	9,4	4,1	2,2	1,7
III	$\text{X} = -\text{CHO}$	10,1	4,9	1,9	0,7
IV	$\text{X} = -\text{CH}(\text{OCOCH}_3)_2$	9,6	4,3	2,1	1,3
V	$\text{X} = -\text{CH}=\text{N}-\text{NH}-\text{CO}-\text{NH}_2$	14,5	7,0	1,1	1,0
VI	$\text{X} = -\text{CH}=\text{N}-\text{NH}-\text{CS}-\text{NH}_2$	14,6	8,2	0,9	0,8
VII	$\text{X} = -\text{CH}=\text{N}-\text{NH}-\text{CO}-\text{CH}_2-\text{CN}$	13,2	7,9	1,4	0,8
VIII	$\text{X} = -\text{CH}=\text{N}-\text{NHCO}-$ 	12,8	7,5	1,6	1,0
IX	$\text{X} = -\text{CH}=\text{N}-$ 	12,5	7,2	1,4	1,0
X	$\text{X} = -\text{CH}=\text{N}-$ 	12,2	7,0	1,5	1,4

\* Number corresponds to number on Fig. 1.

For IIa, X = CHO the electronic spectra are designated as in the work of Saikachi and Ogawa [4] describing the synthesis of similar compounds. The remaining substances described in Table 1 are described for the first time. The synthesis of these compounds was described in a series of communications [3, 5-7].

Study of the optical properties of compounds containing polyene chains, as is well known, has in most recent times attracted attention to investigations in connection with developing a general theory for the color of organic compounds. Comparatively early Hauser and collaborators [8, 9] established the main rules for shifts of absorption maxima in electronic spectra, for the most part of symmetrical polyene systems. In further work Lewis and Galvin [10] and more recently Bayliss, Kuhn, Simpson, and others [11-15] made attempts to substantiate, and in some simple cases also to calculate, both the absorption maximum and the magnitude of its shift by means of molecular orbital methods, beginning with assumptions from quantum-mechanics oscillators and potential functions.

The shift in electronic spectra of asymmetric polyenes has been studied far less. These are much more difficult to calculate. Meanwhile, these systems are more convenient models for studying one of the main questions in the

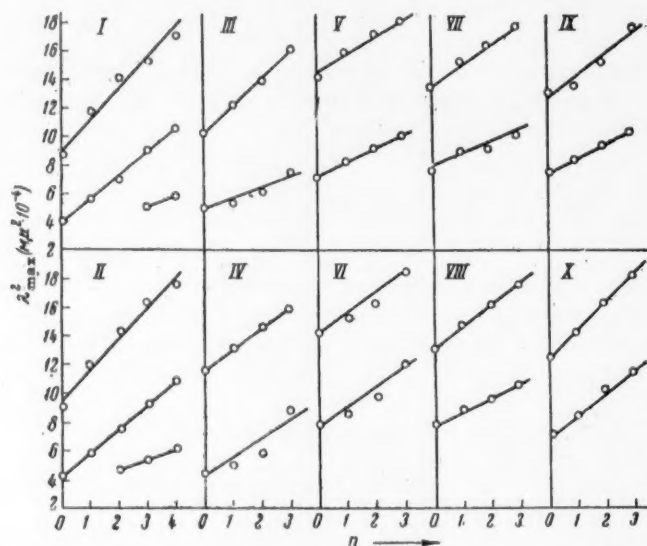


Fig. 1

problem of the coloration of organic compounds, the question of the shift in absorption maxima under the influence of interaction of two previously-mentioned factors: the terminal substituent X and the length of the "conducting" chain of atoms. In all of the 5-nitrofurylpolyenes (IIa) studied, naturally, a regular shift in the main absorption maximum was observed toward longer wave length as a function of increasing number of double bonds. This is applicable both to the two main absorption bands as well as to the third short-wave maximum in those cases in which it can be observed.

We found, that to a sufficiently precise degree the shift of absorption maximum is a function of the number  $\underline{n}$  and the rule is obtained:

$$\lambda_{\max}^2 = a_i + k_i n, \quad (1)$$

where  $\lambda_{\max}$  is the wave length of maximum absorption,  $\underline{n}$  is the number of double bonds in the polyene chain,  $a_i$  and  $k_i$  are constants characteristic of each of the absorption maxima separately, and also for the type substituent X, which are found to be in good agreement with the results of Lewis and Galvin [10]:

$$\lambda_{\max}^2 = k' n, \quad (2)$$

where  $\lambda_{\max}$  is the wave length of maximum absorption,  $n$  is the number of vinylidene groups in the chain, and  $k'$  is a constant equal to

$$k' = \frac{4\pi^2 cm}{k}$$

Here  $m$  is the effective mass,  $k$  is the force constant for a harmonic oscillator, and  $c$  is the speed of light.

Our results are presented in Fig. 1, from which it is seen that in most cases the straight line for long-wave maximum has a greater slope than the straight line for short-wave maxima. In only two cases are parallel straight lines observed. Thus, it is possible to say that  $k_1 \geq k_2 \geq k_3$ .

It is interesting to note that the greater  $k_1$  is, the less  $a_1$  is, that is, the further into the ultraviolet region the high-wave maximum is displaced. This means that as a measure of shift of the long-wave maximum toward the visible region it loses its mobility and reacts weakly to changing length of the polyene chain. The relation found is presented in Fig. 2. The connection between  $a_1$  and  $k_1$  is indicated by the points on the line.

In the work of Lewis and Galvin [10], Hausser and others [8, 9] attention is paid only to the proportionality  $\lambda_{\max}^2 = k'n$ . The physical significance of the constant  $a_1$  was not calculated. Hausser introduced only an assumed empirical "color factor" dependent on the nature of the terminal functional group. It is considered that in the compounds in the references examined by the authors the primary absorption of light is due only to the same polyene chain.

We obtained data on the absorption of compounds in which  $n = 0$ . The light absorption of such compounds relates to an electronic transition of interaction between both terminal functional groups, i.e. the nitrofurane ring and the substituent X, without participation of a conjugated system of vinylidene groups. Thus it was apparent that the points on Fig. 1 corresponding to  $n=0$  did lie on the straight line. From this it follows that the main absorption exists owing to the nitrofurane group and substituent X, but each vinylidene group introduced into the molecule only shifts the absorption maximum by a definite value.

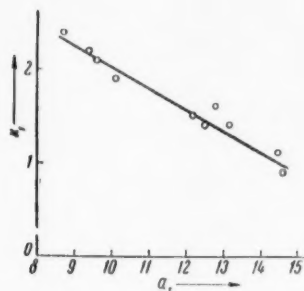


Fig. 2

The large shift of the high-wave absorption maxima on the graphs in Fig. 1 indicates that it is very sensitive to electronic cloud shifts in the polyene chain under the influence of the terminal substituent. The slope of the straight line, i.e. the constant  $k_1$  strongly depends on the nature of substituent X. As is apparent from (2) the constant  $k_1$  is inversely proportional to the coefficient of the harmonic oscillator. In other words, increasing slope of the straight line is evidence for a "loose" system.

These considerations indicate that the long-wave absorption maximum is mainly a function of the substituent X, but the slope of the straight line, i.e. the constant  $k_1$ , must depend to some extent on the electron-donating or electron-accepting properties of substituent X.

The character and amount of shift of the shorter-wave absorption maximum was found to be much more stable both in position and in amount of shift and also considerably less dependent on the nature of the substituent and less sensitive to changing length of the polyene chain. From this it is possible to conclude that this absorption maximum must be due mainly to electronic transitions within the nitrofurane chromophore.

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# CATALYTIC DEMETHYLATION OF ISOMERIC CRESOLS TO PHENOL BY STEAM

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and Yü Chia-yung

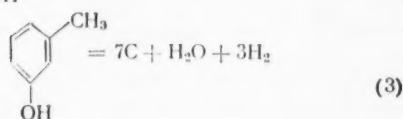
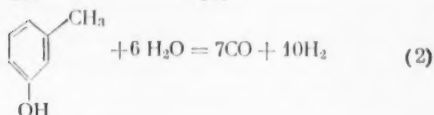
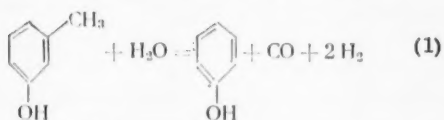
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The conversion of alkyl phenols to phenol is of practical importance because of the great chemical value of the latter. The investigation of this reaction has been described in many reports [1], which may be divided into three groups: 1) thermal dealkylation in the presence of water and hydrogen at 600-800° and atmospheric pressure; 2) homogeneous hydrogenolysis under an initial hydrogen pressure of 100-300 atm and at a temperature of about 500°; 3) catalytic dealkylation in the presence of hydrogen. In the reports of M. G. Gonikberg and Li Kuang-nien [2, 3], who used the second method, it was shown that at 490° and an initial hydrogen pressure of 200 atm the yield of phenol is 29, 12, 7 and 21.3 wt %, calculated on the o-, m- and p-cresols used in the reaction. The yield of catalyst is 81.6, 85.6 and 76.6 wt % respectively. A dehydroxylation reaction takes place at the same time, with formation of 10-20% of benzene and toluene. As a result of work carried out in our laboratory it was established that dealkylation of benzene [4] and pyridine [5] homologs is readily effected on mixed Ni-alumina catalysts and in presence of water. In the present work the demethylation reaction of isomeric cresols was investigated under the same conditions. Table 1 gives some results of the investigation of conversions of m-cresol in the presence of a large excess of water on three Ni-alumina catalysts of different composition. When the experimental data were studied (see below), three possible reactions under these conditions were taken into account.



conditions were taken into account.

During the conversion of organic salts in presence of water, CO and CO<sub>2</sub> are formed; in the majority of our experiment with cresols, a predominant amount of CO was formed, taking account of which, equations (1) and (2) were derived. It may be assumed that reaction (3) is the end result of processes of condensation of cresols, the primary products of which may be anthracene, phenanthrene and other polynuclear aromatic hydrocarbons and their derivatives. The number of hydrogen molecules liberated during these processes, per molecule of initial cresol,  $\bar{n}$ , may vary from 1 to 3. For the calculations we took  $\bar{n} = 2.5$ . For m-cresol the optimum result with respect to extent and selectivity of the demethylation reaction of cresol to phenol was obtained in experiment No. 7 on a catalyst containing ~22% Ni, in the presence of which at a spare velocity of 5 and at 410°, 24 mole % (21.8 wt %) of phenol was formed from the m-cresol employed in the reaction (83.5 % calculated on the reacted m-cresol). With a reduction of the volumetric velocity by 100 % (experiment No. 6), the degree of participation of cresol in the secondary reactions is increased markedly by a corresponding increase in the amount of catalyst: the yield of phenol on the reacted cresol is reduced to 34.5 mole %. The total amount of cresol converted by reactions (1) and (2) - 30.4% in experiment No. 6 and 26.3% in No. 7, 19.7 in No. 28 and 25.33% in No. 35 - depends little on the spare velocity. It may be assumed that principally phenol, formed by reaction (1), takes part in the splitting of the aromatic ring. The velocity of reaction (3) increases considerably with an increase in the contact time (compare experiments No. 6 and 7, 28 and 35).

A temperature increase of 50° in the 410-480° range reduces the relative extent of the demethylation reaction, the selectivity of the catalytic effect falling more markedly with a high nickel content (compare experiments No. 6



TABLE 1. Conversion of *m*-Cresol with Participation of Water on Ni-Alumina Catalysts. Rate of Feed of *m*-Cresol in Experiments No. 6, 7, 16, and 19 = 0.1 ml/min; in Experiments No. 20, 21, and 28 = 0.05 ml/min; in Experiment No. 35 = 0.149 ml/min

Expt. no.	Temp., °C	Volume - tricate of feed of cresol, ml-hour ml-cata- lyst	Amt. of catalyst, ml, and no. of catalyst	H <sub>2</sub> O/C <sub>7</sub> H <sub>8</sub> O, mole	Rate of libera- tion of gas, ml (etc.)	Composition of gas, vol. %				Phenol content in the catalyst, mole, %	Amt. of converted C <sub>7</sub> H <sub>8</sub> O, mole %			Unreacted cresol, mole %	In mole % on unconverted cresol		
						CO <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>		To phenol reaction (1)	By reaction (2)	By reaction (2)		phenol	Reaction product (2)	Reaction product (3)
6	409	0,62	9,7;	36:1	74,0	8,05	22,3	68,5	1,2	22,1	45,6	14,8	14,8	54,8	34,5	32,8	32,8
7	410	1,25	4,8;	36:1	25,1	7,0	24,3	67,2	1,5	25,1	23,8	2,54	2,55	71,5	83,5	8,7	7,9
16	426	0,6	10;	36:1	14,3	12,3	16,4	69	2,3	13,2	7,8	1,97	2,33	87,9	65	16,1	19
19	476	1,2	5;	36:1	43,7	12,3	16,4	69	2,3	13,2	12	4,5	5,15	79,35	56	21	21
20	464	0,6	5;	72:1	64	12,8	14,3	73	—	19,1	6,5	26,6	40,5	26,7	8,55	36,3	55,2
21	464	0,6	5;	72:1	14,3	10,7	16,3	73	—	31,5	29	1,81	6,05	63,1	78,5	4,92	16,3
28	439	1,2	2,5;	440:1	40,2	10	9,4	76	4,6	15,2	22	14,1	52,5	28,6	7,04	19,2	7,3
35*	443	2,32	5,0;	30:1	57,6	13,35	14,1	66,2	6,43	23,9	22	3,33	4,37	67,3	67,5	10,2	13,35

\* 9% of the reacted cresol was converted to benzene and toluene.

and 20, 16 and 19). Partial poisoning of the catalyst by carbon deposits increases its activity and selectivity with respect to reaction (1). Experiment No. 21 was carried out with the catalyst used in experiment No. 20; between the experiments the catalyst was removed from the reaction tube and cooled. The selectivity of its effect increased in this case from 8,55 to 78,5%, the conversion of cresol to phenol in experiment No. 21 was 31,5% compared with 19,1% in experiment No. 20. The dehydroxylation reaction of cresol in the presence of water becomes appreciable only on a catalyst with a high Ni content: the reaction products in experiment No. 35 contain about 10 mole % of benzene and toluene, calculated on the reacted cresol.

Table 2 compares the results of experiments carried out with *m*-, *p*- and *o*-cresols. The reactivity of *o*- and *p*-cresols differs markedly from the behavior of *m*-cresol under the same conditions. The selectivity of the course of the demethylation reaction is reduced from 67,5% for *m*-cresol to 13,9 and 21,1% for *p*- and *o*-cresols, principally as a result of the marked increase in the velocity of the condensation processes (reaction (3)). The rate of complete destruction (reaction (2)) also increases approximately 2-fold for *p*-cresol and 4-fold for *o*-cresol as against the destruction rate of the ring for *m*-cresol. The conditions under which *m*-cresol is demethylated with good yields are quite unsuitable for the *p*- and *o*-isomers. A reduction in temperature from 440 to 415° increases considerably the phenol yields from *o*- and *p*-cresols.

## EXPERIMENTAL

The experiments were carried out in an automated catalytic apparatus of the circulating type, described in [6], with detachable reactors [7]. Catalysts with the composition Ni/Al<sub>2</sub>O<sub>3</sub> = 1:1 (No. 1), 1:2 (No. 2) and 1:4 (No. 3) were prepared by N. D. Zelinskii's method [8]. The cresol: water ratio varied from 30 to 70 in different experiments, and therefore the partial pressure of cresol was 10-25 mm Hg. Gas-liquid and absorption chromatography methods were used for analysis of the liquid and gaseous reaction products. The use of gas-liquid chromatography for the quantitative analysis of mixtures of phenols was investigated in detail by Janak [10], Socol [11], Bergmann [12], and others. In this work we analyzed the catalysate in a column of length 2 m and diameter 4,5 mm, packed with diatomite brick (particle size 0,25-0,5 mm). Methylphenyl polysiloxane (30 wt %) was applied to the brick as the stationary phase. 7g of methylphenyl polysiloxane was required to pack the column. Nitrogen was used as the gas-carrier. For the analysis we took about 20g of the mixture, which was introduced into the column by means of a syringe through a rubber cap at the top of the column. Measurement was carried out in a thermal conductivity cell, consisting of two parallel glass

tubes with 0.04 mm diameter platinum filaments drawn out along the tube axis, the resistance of each filament being 14  $\Omega$ . The detector signals were recorded on an EPP-09. For detection at room temperature we used the method of preliminary conversion to hydrogen of the vapors of the substances after they had been separated in the chromatographic column [12, 13]. For both classes of substance, not only phenol and its homologs, but also the aromatic hydrocarbons, with the exception of the *m*- and *p*-isomers, were clearly separated in the chromatographic column employed. A preliminary check on artificial mixtures showed that in the great majority of experiments the absolute analytical error did not exceed 0.5-1%. Chromatograms of the analyses of experiments No. 21 and 41 are given in Fig. 1 and 2.

The analysis of the gaseous products was carried out in a VTI apparatus ( $\text{CO}_2$ , CO and  $\text{H}_2$ ) and in a 6-m long chromatographic column, filled with aluminum oxide, in a current of  $\text{CO}_2$  with development of the components with 40% KOH (hydrocarbons  $\text{C}_1 - \text{C}_4$ ). The study of the results was carried out from the analytical data by means of the following equations:

$$m = \gamma \cdot 100 + m_2 + m_3; \quad V_{\text{CO}}/22400 = F \gamma + 7m_2;$$

$$V_{\text{H}_2}/22400 = 2F \gamma + nm_3 + 10m_2 - (B + T)\gamma,$$

where  $m$  is the amount of cresol (g-mole) fed per min;  $\gamma$  is a conversion factor for the results of the chromatographic analysis of the liquid catalysate;  $V_{\text{CO}}$  and  $V_{\text{H}_2}$  are the volumes of CO and  $\text{H}_2$  (ml) liberated per min;  $m_2$  and  $m_3$  is the amount of cresol (g-mole) converted by reactions (2) and (3) respectively per min;  $F$  is the percent of phenol in the catalysate;  $(B + T)$  is the percent of benzene and toluene in the catalysate. To simplify the calculation the composition of the gaseous products was reduced to a two-component system ( $\text{CO} + \text{H}_2$ ) by corresponding replacement of the other components by CO and  $\text{H}_2$ .

TABLE 2. Conversions of *m*-, *o*- and *p*-Cresols with Participation of Water on 1 : 1 Ni/  $\text{Al}_2\text{O}_3$  Catalyst (No. 1) (volume of catalyst 5 ml; rate of feed of cresols 0.194 ml/min, water 0.9 ml/min)

Expt. No.	Temp., °C	Rate of liberation of gas, ml/ min (etc.)	Composition of the gas, vol. %						Phenol content of the catalyst, %	Amount of converted $\text{C}_7\text{H}_8\text{O}$ , mole %				Amount of unre-acted cresol, mole %	Amount, calc. on the converted cresol, mole %		
			$\text{CO}_2$	CO	$\text{H}_2$	$\text{CH}_4$	$\text{C}_2\text{H}_4$ and $\text{C}_3\text{H}_6$	$\text{C}_3\text{H}_8$		to phenol	by reac- tion (2)	by reac- tion (3)	phenol		reaction product (2)	reaction product (3)	
m - Cresol																	
35	443	57.6	13.35	14.1	66.2	6.43	Not determ.	23.9	22	3.33	4.37	67.3	67.5	10.2	13.35		
p - Cresol																	
37	441	58.1	4.62	16.6	75.8	1.25	Not determ.	11.2	6.6	7.65	33	52.5	13.9	16.2	70		
38	413	31.4	4.3	15	79	1.1	The same	9.1	7.9	1.2	11.9	79	37.6	5.8	56.5		
o - Cresol																	
41	442	97	7	11	74	—	5.3	2.7	26.2	13.3	12.7	36.4	37	21.1	20.3	57	
42	415	70.5	7.2	10.3	72	—	5.0	5.65	23.1	17.3	2.34	21.6	57.5	40	7.9	52.1	

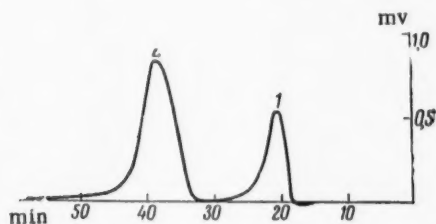


Fig. 1. Chromatogram of the catalysate from experiment No. 21: 1) phenol; 2) *m*-cresol.

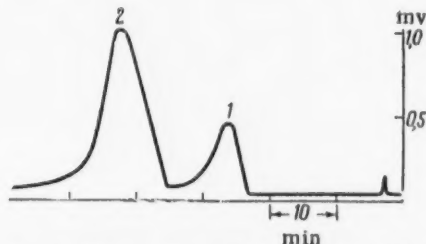


Fig. 2. Chromatogram of the catalysate from experiment No. 41: 1) phenol; 2) *m*-cresol.

Therefore it was shown that in the 410-470° temperature range in the presence of a large excess of steam, isomeric cresols are demethylated on Ni-alumina catalysts to phenol. The optimum result for m-cresol - phenol yield 24 mole % calculated on the cresol fed, and 83.5% on the decomposed cresol - was obtained at a temperature of 410° on 1 : 2 Ni/ Al<sub>2</sub>O<sub>3</sub> catalyst at a volumetric feed rate of cresol equal to 1 : 25. The behavior of o- and p-cresols under the selected reaction conditions differed markedly from that of m-cresol: the secondary condensation reaction, with formation of tarry and carbonaceous substances, and the splitting reaction of the benzene ring acquire a much greater velocity.

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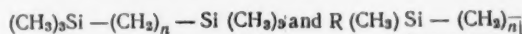
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# ORGANOSILICON COMPOUNDS WITH HYDROGEN BRIDGES BETWEEN THE SILICON ATOMS THERMAL CONVERSIONS

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Acad. Sci. USSR A. D. Petrov

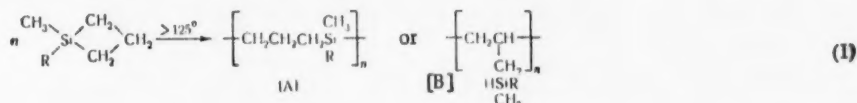
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Translated from Doklady Akademii Nauk SSSR, Vol. 141, No. 4,  
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Original article submitted August 17, 1961

In [1] we investigated thermal conversions of the  $\text{Si}(\text{CH}_3)_n\text{Si}$  group in a circulating system at  $600^\circ$ . Under these conditions the bridge group in  $\alpha, \omega$ -hexamethyldisilylalkanes  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{Si}(\text{CH}_3)_3$  is split when  $n \geq 2$ , but is retained when  $n = 1$ , but a methyl radical or hydrogen is removed. In the present work we investigated the effect of elevated temperatures on bridge compounds at temperatures up to  $400^\circ$  in sealed ampoules. By way of compounds containing a bridge group, we investigated substances of the type

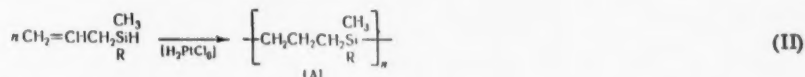


It was found that  $\alpha, \omega$ -hexamethyldisilylalkanes with  $n = 2, 3, 4$  do not undergo a change in properties at  $350$ - $360^\circ$  with a heating residence time of 3 hours or even longer, and that 5- and 6-membered cyclanes are not less stable under these conditions. In particular, 1,1-dimethylsiliconcyclopentane is stable at  $390^\circ$  (3 hours). In contrast to these cyclanes, four-membered compounds were polymerized when heated: 1-methyl-1-chlorosiliconcyclobutane, commencing at  $170$ - $180^\circ$ , and 1,1-dimethylsiliconcyclobutane at  $125$ - $130^\circ$ . As a result of the reaction, solid, elastic substances soluble in the initial monomers and in benzene and chloroform were obtained.

Polymers with the same elementary composition as the initial siliconcyclobutanes may be assumed to have structures (A) or (B)

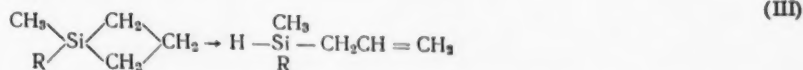


A comparison of the infrared spectra\* of the polymers we obtained by reaction (I) and cross synthesis by reaction (II) [3]:



showed that they were completely identical. At the same time, the spectrum\*\* of the polymer prepared from 1,1-dimethylsiliconcyclobutane was different from the spectrum of the polymer of structure (B), given in [4]. These data enabled us to select structure (A) for the polymer obtained.

There is little probability that in reaction (I), isomerization (III) of siliconcyclobutanes to allyl silanehydrides precedes the formation of a linear polymer.



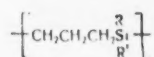
\* The infrared spectra were determined in an IKS-10 double-beam apparatus in the  $400$ - $2400$  and  $2750$ - $3100 \text{ cm}^{-1}$  range.

\*\* A frequency in the  $2000$ - $2200 \text{ cm}^{-1}$  range, attributed to the  $\equiv \text{S}-\text{H}$  bond and generally very strong, was completely absent from this spectrum.

In point of fact, in a control experiment we established that  $\text{H-Si}(\text{CH}_3)(\text{R})-\text{CH}_2\text{CH}=\text{CH}_2$  is not appreciably polymerized at 180-200°, whereas under these conditions  $\text{Cl}(\text{CH}_3)_2\text{Si}-(\text{CH}_2)_3-$  was completely converted to the polymer. Moreover, an infrared analysis of the monomer distilled from the incomplete polymerization of  $\text{Cl}(\text{CH}_3)_2\text{Si}-(\text{CH}_2)_3-$  showed that it did not contain admixtures of hydride-containing compounds.

The cause of the difference in the behavior of siliconcyclobutanes and 5- or 6-membered siliconcyclanes at elevated temperatures must evidently be explained by the strain of the 4-membered ring [5, 6]. It is known, for example, that when siliconcyclobutanes are treated with alcoholic alkali or concentrated sulfuric acid (followed by treatment with water) the rings are opened, forming sym-dipropyltetraalkyldisiloxanes, far more readily than 5- or 6-membered rings [6].

It must be noted that in contrast to known [3, 4, 7, 8] methods of obtaining linear polymers of the type



the method of thermal polymerization of siliconcyclobutanes makes it possible to obtain very high-molecular products.

5- and 6-membered cyclanes were obtained by known methods [9, 10].

1-Methyl-1-chlorosiliconcyclobutane. 212 g of  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiCl}_2(\text{CH}_3)$  and 30 g of Mg in 500 ml of ether were boiled with stirring for 12 hours. After the precipitate and magnesium had been separated, the filtrate was distilled. 151 g of trichloride was recovered and 26 g of crude  $\text{Cl}(\text{CH}_3)_2\text{Si}-(\text{CH}_2)_3-$  with a b. p. of 105-109° was obtained. The yield was 68% on the trichloride used. After distillation in a column with 10 theoretical plates the analytically pure substance had the following properties: b.p. 106°/738 mm;

$n_D^{20}$  1.4490;  $d_4^{20}$  0.9858.  $\text{MR}_D$  found - 32.8, calculated 32.4.  
Found Cl 21.13%, calculated Cl 21.09%.

Rotation-vibration spectrum\*: 151 (3), 177 (7 w), 203 (8 v.w.), 241 (7 w), 394 (10), 433 (8 w), 553 (2), 639 (5 w), 678 (4 w), 721 (3 w), 771 (1), 825 (1), 874 (4), 901 (9), 925 (3), 1128 (5), 1217 (1), 1260 (0), 2936 (9 w), 2985 (10 w).

1,1-Dimethylsiliconcyclobutane was obtained by the usual method from  $\text{CH}_3\text{MgBr}$  (9 g of Mg) and 31 g of  $\text{Cl}(\text{CH}_3)_2\text{Si}-(\text{CH}_2)_3-$  in 100 ml of ether, the yield being 17 g, equal to 65%; the b.p. was 82-83°/740 mm;

$n_D^{20}$  1.4260;  $d_4^{20}$  0.7702;  $\text{MR}_D$  found 32.6; calculated 32.8.

Rotation-vibration spectrum\*: 151 (2); 189 (6 w); 217 (7); 239 (5); 450 (10 r); 614 (9 w); 649 (5); 690 (2); 706 (3); 728 (4); 810 (5 w); 886 (5 w); 908 (8 w); 931 (4); 1066 (0); 1125 (4); 1195 (2); 1219 (2); 1255 (2); 1327 (1); 1417 (6 v.w); 1454 (1); 2860 (0); 2908 (10 w); 2934 (4); 2971 (1 r.w).

Literature data [11]: b.p. 81°/730 mm;  $n_D^{20}$  1.4270,  $d_4^{20}$  0.7746.  $\text{MR}_D$  found 32.2.

Frequencies characteristic of Si-H or C=C-bonds were not noted in the spectra of either of the above-described siliconcyclobutanes. In these spectra, and in the rotation-vibration spectra of  $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{Si}-(\text{CH}_2)_3-$ , synthesized in [12], a stable combination of frequencies was noted: a very intense line in the 430-450  $\text{cm}^{-1}$  region, and lines in the 725, 815, 878, 903, 927 and 1125  $\text{cm}^{-1}$  regions, which evidently characterize the siliconcyclobutane group.

Allylmethylchlorohydrosilane. To 50 g of Mg in 1 liter of ether was added 2 ml of allyl bromide; after the reaction had commenced, a mixture of 120 g of allyl bromide and 172 g of methyl dichlorosilane was added in such a way that intense boiling of the ether was continuous. After the precipitate had been separated by double distillation (in a column with 20 theoretical plates),  $\text{CH}_2=\text{CHCH}_2\text{SiClH}(\text{CH}_3)$  was obtained with a yield of 13% on the  $\text{CH}_3\text{SiCl}_2\text{H}$  taken; the b.p. was 94-95°/755;

$n_D^{20}$  1.4310,  $d_4^{20}$  0.9175.  $\text{MR}_D$  found 34.0, calculated 34.5.

\*In all cases the rotation-vibration spectra were determined in an ISP-51 apparatus with a central chamber; the intensities are given in a 10-point visual scale.



Rotation-vibration spectrum: 198 (3 w); 210 (3); 240 (1); 280 (0); 407 (3 w); 496 (7 w); 588 (4 w); 656 (1); 688 (3); 722 (1); 742 (2); 769 (1); 797 (0); 851 (v. w.); 907 (2); 940 (1); 995 (1); 1165 (6 w); 1190 (2 w); 1239 (g); 1253 (0); 1301 (8 r); 1392 (3); 1419 (3); 1635 (10); 2175 (9 w); 2890 (2 w); 2908 (9); 2974 (5); 3003 (6); 3080 (4).

The frequencies 407, 940, 995, 1165, 1300, 1392, 1635, 3003, and 3080  $\text{cm}^{-1}$  characterize the allyl group combined with silicon, while the 2175  $\text{cm}^{-1}$  line characterizes the  $\equiv \text{Si} - \text{H}$  bond [13].

The polymer  $-\text{[Cl(CH}_3\text{)SiCH}_2\text{CH}_2\text{CH}_2\text{]}_n$ . When 6 g of  $\text{CH}_2 = \text{CHCH}_2\text{SiCl(CH}_3\text{)H}$  was heated with 1 drop of 0.1 N  $\text{H}_2\text{PtCl}_6$  in isopropyl alcohol to 80° the reaction took place exothermically, after which the mixture was heated for 1 hour at 140-150°C. The polymer was distilled at 100° and 2 mm for 2 hours. The yield of polymer was ~60%; it was a brittle paraffin-like mass with an m.p. of 60-65°, readily soluble in benzene and  $\text{CCl}_4$ .

The thermal tests were carried out in ampoules\* in which a 1.5-2 ml sample of the substance was introduced, after which the air was displaced by dry nitrogen and the ampoule was sealed. The thermal stability was measured in a case where the external appearance, specific gravity and the  $n_D^{20}$  of the substance were practically unchanged.

A  $(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3$  sample, heated for 3 hours, was converted to solid polymer at 230°. To obtain a 1-2% solution of this polymer in benzene, 24-36 hours were required for swelling of the polymer and after a brief shaking it dissolved completely. It was precipitated as a sticky lumpy mass by a double volume of methanol. After vacuum distillation at 100°/2 mm for 3 hours the yield was > 85%. When the polymer was heated in air to 70° it became completely transparent, and at 160-180° was converted to a very viscous liquid. In external appearance, films of this substance obtained by removal of the solvent from benzene solutions of the polymer resembled polyethylene films, but were more elastic. They were used for determining the infrared spectra, which were compared with the spectra of the polymer  $-\text{[(CH}_3\text{)}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{]}_n$ , given in [4]. The reprecipitated polymer was analyzed:

Found %: C 60.39; 60.15; H 11.99; 11.83; Si 27.90; 28.19  $\text{SiC}_5\text{H}_{12}$ .

Calculated %: C 59.90; H 12.06; Si 28.02.

The polymer of 1-methyl-2-chlorosiliconcyclobutane obtained at 230° was a transparent rubber-like substance which hydrolyzed in air.

Found %: Si 23.54; 24.02  $\text{SiC}_4\text{H}_9\text{Cl}$ . Calculated %: Si 23.25.

If polymerization of siliconbutanes was carried out at temperatures close to the initial polymerization temperatures for 5-20 minutes, the contents of the ampoule were a viscous liquid consisting principally of unreacted monomer and a small amount of polymer, similar in external appearance to that described above.

The authors wish to express their gratitude to L. A. Leites, who carried out the spectral part of the investigations in this work.

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\* Pyrex glass.

INVESTIGATION OF THE MECHANISM OF THE REACTION  
OF ARYL NITROSO COMPOUNDS WITH HYDRAZOIC ACID  
BY MEANS OF  $N^{15}$

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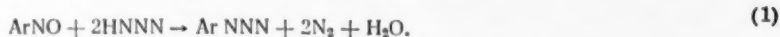
(Presented by Academician M. M. Shemyakin, April 19, 1961)

Translated from Doklady Akademii Nauk SSSR, Vol. 141, No. 4,

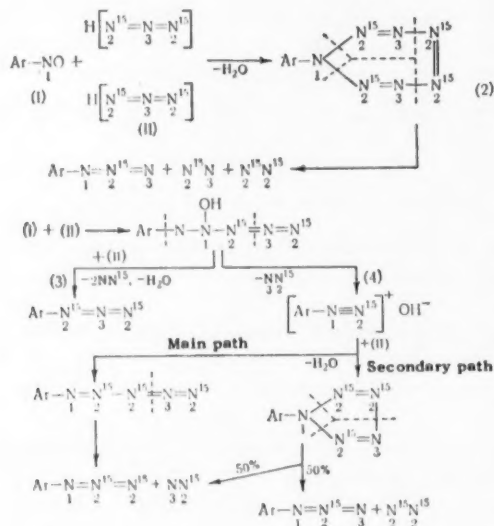
pp. 847-850, December, 1961

Original article submitted July 4, 1961

Until recently the mechanisms of the formation and reaction of triazo compounds have been little investigated. A number of important problems in this field were only recently solved by Clusius and his co-workers. In particular, the linear structure of the azide group and the non-equivalence of its component nitrogen atoms were accurately established [1]. A knowledge of this assists in turn the study of the mechanism of the reactions and formation of azides. A new method of obtaining aryl azides was recently published [2]. Aromatic nitroso compounds are reacted with hydrazoic acid with gentle heating and aryl azides form smoothly with liberation of elementary nitrogen.



The authors of [2] limit themselves to the assumption of intermediate formation of a diazo hydroxide, but they give no experimental proof of this. Therefore the reaction mechanism is obscure. Three reaction mechanisms

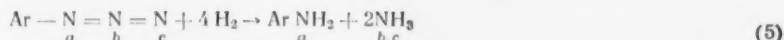


differing by the position of the initial nitrogen atoms in the reaction products, may be assumed. Here, the use of the nitrogen isotope  $N^{15}$  would obviously make it possible to determine the correct reaction path.

If hydrazoic acid  $\text{HN}^{15}\text{NN}^{15}$  were used, the distribution of  $N^{15}$  in the reaction products would correspond to systems (2) - (4).

In mechanism (4), according to Clusius [3] the second stage has a branched character and the expected results may be calculated on the basis of his data.

The reactions were carried out with hydrazoic acid labeled with  $N^{15}$  at the terminal nitrogen atoms. A current of carbon dioxide was passed through a reaction flask containing an alcoholic solution of the nitroso compound. After complete removal of air, a solution of  $HN_3$  in chloroform was added, the flask was heated gently and the liberated nitrogen was collected over a caustic potash solution, transferred to evacuated ampoules and analyzed in a mass spectrometer. The aryl azides were precipitated in the pure form and were converted to the amine and ammonia by reduction with zinc dust and hydrochloric acid [4]



The reaction products were separated, converted to elemental nitrogen and analyzed in a mass spectrometer. The analytical results are given in Table 1.

TABLE 1

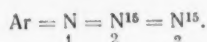
Expt. no.	$N^{15}$ content in the initial substances (%)	Found			Calculated with respect to mechanism (2), (3), and (5)		
		$\text{Ar}-\text{N}=\text{N}=\text{N}$ $a \quad b \quad c$		NN	$\text{Ar}-\text{N}=\text{N}=\text{N}$ $a \quad b \quad c$		NN
		$\text{ArNH}_2$ $a$	$2\text{NH}_3$ $b, c$		$\text{ArNH}_2$ $a$	$2\text{NH}_3$ $b, c$	
1	$p\text{-NO}_2\text{-Ph-NO}$ $\text{H}[\text{N}=\text{N}=\text{N}]$ (0,37) (0,37) (4,95) (0,37) (4,95)	0,40	4,86	3,10	0,37(2) 4,95(3)	2,66 2,66	3,8 2,66
2	$p\text{-CH}_3\text{-CO-NH-Ph-NO}$ $\text{H}[\text{N}=\text{N}=\text{N}]$ (0,37) (0,37) (4,95) (0,37) (4,95)	0,39	4,72	3,00	0,37(4) 0,37(2) 4,95(3)	4,83 2,66 2,66	2,73 3,8 2,66
3	$p\text{-Cl-Ph-NO}$ $\text{H}[\text{N}=\text{N}=\text{N}]$ (0,37) (4,27) (0,37) (4,27)	—	3,9	2,50	—	4,71 2,32(2) 2,32(3)	2,80 3,30 2,32
4	$p\text{-(CH}_3)_2\text{N-Ph-NO}$ $\text{H}[\text{N}=\text{N}=\text{N}]$ (0,37) (0,37) (4,27) (0,37) (4,27)	—	—	2,55	—	3,98(4) —	2,47 3,30(2) 2,32(3) 2,58(4)

When *p*-nitrophenyl azide and *p*-acetaminophenyl azide are reduced, ammonia and *p*-phenylene diamine are obtained. An analysis of the latter gives the total  $N^{15}$  content in both nitrogen atoms. Since it is known beforehand that one amino group originating from the substituent and not a participant in the reaction cannot contain an excess of  $N^{15}$ , Table 1 gives the converted  $N^{15}$  content in the single amino group corresponding to the nitrogen from the C-N bond of the azide group.

The values calculated for mechanism 4 were obtained on the basis of the results of Clusius' work [3]. Of the substances we investigated, a calculation according to Clusius may be made only for *p*-nitrophenyl azide. In other cases a comparison was made with the results for analogous compounds. Thus, *p*-chlorophenyl azide was compared with *p*-bromophenyl azide, and *p*-dimethylaminophenyl azide with *p*-ethoxyphenyl azide. For *p*-acetaminophenyl azide the ratio of the reaction paths was first calculated from the ammonia analysis, and the  $N^{15}$  content in the nitrogen was then calculated from this ratio.

To check the absence of secondary reactions with liberation of nitrogen, samples of the latter were taken at the beginning and end of the experiment for mass-spectrometric analysis. The isotopic composition of the nitrogen was practically constant throughout the reaction.

There was no excess of  $N^{15}$  in the amine obtained by reduction of the aryl azide. Therefore, in the azide the nitrogen adjoining the ring is lightly attached. In the ammonia obtained from the other two N atoms of the azide, the  $N^{15}$  content almost reaches the initial concentration. Therefore both these atoms are heavy and originate from the terminal atoms of the nitrogen of the azide ion. The isotopic structure of the aryl azide corresponds therefore to



Azide with this structure may be obtained only by system (4). The somewhat lesser content of  $N^{15}$  than in the initial nitrogen may be explained by the fact that in the second stage the reaction takes place by a branched mechanism,

as a result of which, azide with the structure  $\text{Ar}-\text{N}_1=\text{N}_2^{15}=\text{N}_2^{15}$  is formed to some extent. Therefore, the isotopic composition of the central N atom in the azide group corresponds exactly to the isotopic composition of the end nitrogen atoms in the azide ion. The end N atom contains a lesser amount of  $\text{N}^{15}$ , which may be calculated if the degree of branching of the reaction for the corresponding substituent is known.

TABLE 2

Initial nitroso compound	Proportion of the path of the reaction %	
	of the main reaction with formation of linear pentazene	of the secondary reaction with formation of cyclic pentazene
$\text{p-NO}_2\text{PhNO}^*$	92 (92)	8 (8)
$\text{p-CH}_3\text{CONHPhNO}^*$	80 —	20 —
$\text{p-ClPhNO}^*$	62 (71)***	38 (29)
$\text{p-(CH}_3)_2\text{NPhNO}^{**}$	53 (47)****	47 (53)

\* Calculated with respect to the ammonia composition.

\*\* Calculated with respect to the nitrogen composition.

\*\*\* Clusius' data for  $\text{p-BrPhN}_2^+$ .

\*\*\*\* Clusius' data for  $\text{p-C}_2\text{H}_5\text{OPhN}_2^+$ .

In some of the experiments the  $\text{N}^{15}$  content in the nitrogen did not correspond completely to the calculated. For the moment, this is difficult to explain.

The proportion of both reaction paths in the second stage of the process was calculated from the isotopic composition of the products. These values are given in Table 2 and are compared with the branching of the reaction of diazo compounds (having the same or similar substituents) with hydrazoic acid according to Clusius' data.

The calculation was made by means of the formulae:

$$k = 2x - 100;$$

$$l = 2(100 - x),$$

where  $k$  is the proportion of the main reaction (%),  $x$  is the proportion of the main product (%),  $l$  is the proportion of the secondary reaction (%). The percent

of the main product ( $x$ ) was calculated, for example, with respect to  $\text{p-acetaminophenyl azide}$ , from the equation:

$$4,95x + \frac{4,95 + 0,37}{2}(1 - x) = 4,72.$$

Assuming that the errors of the mass-spectrometer determination are up to 3% of the relative errors, the errors in the proportions of the reaction paths may be assessed as  $\pm 10\%$ . Clusius' data are evidently accurate up to  $\pm 4\%$ . Taking into account further that the substituents are different, the values and order of the figures may be considered fairly close.

As may be seen from Table 2, the degree of participation of the main reaction increases with an increase in the electrophilic character of the substituent. Substituents influence in the same direction the activity of diazo cations during coupling. This analogy is understandable because both reactions include an electrophilic attack of the diazo cation by the terminal nitrogen atom on the second reacting molecule. During a diazo reaction the first stage — the formation of linear or cyclic pentazene — is the determining velocity. During the reaction of nitroso compounds with hydrazoic acid the diazo reaction is the second stage and takes place far more rapidly than the first, i.e. the formation of a diazo cation. This follows from [9], where it was shown that an intermediate product is not formed when an inadequate amount of hydrazoic acid is present (less than 2 moles per 1 mole of nitroso compound), but that the expected amount of end products and part of the unchanged nitroso compound are obtained.

The reaction velocity increases from  $\text{p-nitrosodimethylaniline}$  to  $\text{p-nitrosonitrobenzene}$ , i.e. it also depends on substituents, like the velocity of the diazo reaction investigated by Clusius. Although the slow stages of these reactions are different, such analogies must be expected because the formation of diazo compounds must assist an increase in the positive charge on the nitrogen of the nitroso group, caused by electrophilic substituents.

We wish to express our thanks to Academician of the Ukrainian SSR, A. I. Brodskii, for his help in this work.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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## INVESTIGATION OF SELENOCYANATE COMPLEXES OF COBALT AND NICKEL

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(Presented by Academician I. I. Chernyaev, July 1, 1961)

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Hitherto, cobalt and nickel selenocyanates have been little investigated [1]. In the literature, only the results of preparative investigations by Spacu [2, 3] on amino complexes of these metals with  $\text{SeCN}^-$  ions in the outersphere are given. We set ourselves the task of investigating the formation of selenocyanate complexes of nickel and cobalt in different solvents and synthesizing simple nickel and cobalt selenocyanates and their molecular compounds containing  $\text{SeCN}^-$  ions in the inner sphere.  $\text{NaSeCN}$  and  $\text{KSeCN}$  (synthesized as described in [4]), cobalt and nickel perchlorates (obtained by the action of perchloric acid on the corresponding carbonates [5]) served as the initial compounds in our investigations. By way of solvents we used water, methanol and acetone. These were thoroughly purified, the last two being dehydrated. The initial concentrations of sodium and potassium selenocyanates were determined with respect to selenium; cobalt gravimetrically (gravimetric form of  $\text{CoSO}_4$ ), nickel by means of dimethylglyoxime. Since nickel and cobalt salts were used in the form of crystallohydrates in this work, the moisture concentration was kept constant (less than 0.5 vol %) in a series of experiments during the investigation of non-aqueous solutions.

Aqueous solutions of selenocyanates of cobalt, and particularly of nickel, are unstable. The solutions are more stable if they contain an excess of the nickel or cobalt salt with respect to the selenocyanate ion. This indicates the greater strength of the simplest  $\text{CoSeCN}^+$  and  $\text{NiSeCN}^+$  complexes. Their composition was established spectrophotometrically at 510  $\text{m}\mu$  (in the case of cobalt) and 330  $\text{m}\mu$  (for nickel). In composition,  $\text{CoSeCN}^+$  and  $\text{NiSeCN}^+$  resemble the corresponding thiocyanates [6, 7]. In aqueous solutions, for  $\text{CoSeCN}^+$  we succeeded in determining the dissociation constant potentiometrically. To measure the equilibrium concentrations of  $\text{SeCN}^-$  ions we used an indicator electrode of the second order  $\text{Ag}/\text{AgSeCN}$ . The dissociation constant of  $\text{CoSeCN}^+$  ( $K = 6.8 \cdot 10^{-2}$ ) is of the same order as for  $\text{CoCNS}^+$ . We did not succeed in determining the dissociation constant of  $\text{NiSeCN}^+$  as a result of the rapid decomposition of the solutions.

The reaction between  $\text{SeCN}^-$  and ions of the corresponding metals in methanol was investigated by the method of electrical conductivity and spectrophotometry. During the investigation of isomolar series of solutions of  $\text{Co}(\text{ClO}_4)_2 - \text{NaSeCN}$ , and  $\text{Ni}(\text{ClO}_4)_2 - \text{NaSeCN}$  by the electrical conductivity method, a diffuse minimum is found on the composition - property graph (the electrical conductivity of pure salts in methanol varies linearly), indicating the formation of  $\text{Me}(\text{SeCN})_3^-$  and  $\text{Me}(\text{SeCN})_4^-$  complexes.

A more complete picture of complexing can be obtained spectrophotometrically. Methanol solutions of  $\text{Co}(\text{ClO}_4)_2$  containing a slight excess of  $\text{SeCN}^-$  ions are characterized by the presence of two maxima at 520 and 630  $\text{m}\mu$ . With an increase in the  $\text{SeCN}^-$  concentration the first maximum decreases, while the second one increases. Measurement of the optical density of isomolar series of solutions showed that for cobalt - irrespective of the initial concentrations of the components, which varied from 0.05 to 0.5 mole/liter - at  $\lambda = 520 \text{ m}\mu$  only the complex  $\text{CoSeCN}^+$  may be detected. A methanol solution of  $\text{Ni}(\text{ClO}_4)_2$  has an absorption maximum in the 400  $\text{m}\mu$  region. With addition of  $\text{NaSeCN}$  the optical density of  $\text{Ni}(\text{ClO}_4)_2$  solutions increases markedly (particularly in the 320-330  $\text{m}\mu$  region). The 400  $\text{m}\mu$  band is also retained on the light-absorption curve of these solutions, but its intensity is appreciably higher, however, than for pure  $\text{Ni}(\text{ClO}_4)_2$ . Taking this into account, we measured the optical densities of isomolar series of solutions at 320 and 400  $\text{m}\mu$ . It was found that by varying the initial concentrations of the components the  $\text{NiSeCN}^+$ ,  $\text{Ni}(\text{SeCN})_2$  and  $\text{Ni}(\text{SeCN})_3^-$  complexes may be revealed.

It was naturally assumed that the more complex complexes could be detected with a large excess of addend. Therefore we measured the optical density of solutions with a constant concentration of the central ions and an increasing  $\text{SeCN}^-$  ion concentration. The data obtained were examined by the Bjerrum method [8]. Measurement of the optical density was carried out at 630 m $\mu$  (for cobalt) and 320 m $\mu$  (for nickel). A "formation curve" was plotted on the basis of the data obtained. As may be seen from Fig. 1, for nickel the maximum value  $\bar{n} = 4$ , for cobalt  $\bar{n} = 6$ . Our data agree with those of West [9], who showed the formation of  $\text{Co}(\text{CNS})_6^{4-}$  in aqueous-alcoholic solution.

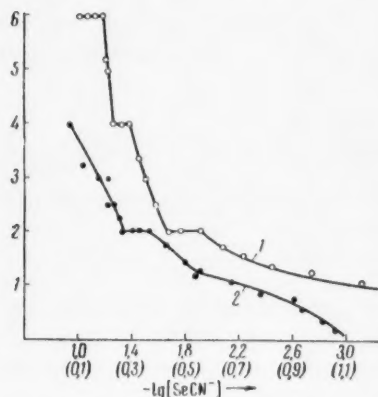


Fig. 1. Formation curves in the system  $\text{Me}^{2+} - \text{SeCN}^- - \text{CH}_3\text{OH}$ . 1) Cobalt salt; 2) nickel salt (the figures in brackets on the abscissa refer to 1).

From the "formation curve" we found the approximate dissociation constants (indicated at the beginning by a series of steps) and then calculated the total dissociation constants of the corresponding complexes (see Table 1). The dissociation constant of  $\text{CoSeCN}^+$  was found by the N. P. Komar' method [6].

The formation reaction of complexes takes place more readily in acetone solutions than in methanol solutions. This can be shown by measuring the electrical conductivity of the isomolar series  $\text{Co}(\text{ClO}_4)_2 - \text{NaSeCN}$ ,  $\text{Ni}(\text{ClO}_4)_2 - \text{NaSeCN}$ , and also  $\text{Co}(\text{SeCN})_2 - \text{KSeCN}$ . In this case the  $\kappa$ -composition curve has a minimum, indicating the formation of  $\text{Me}(\text{SeCN})_3^-$  complexes. As was established for thiocyanates [10], spectrophotometry of isomolar series in acetone makes it possible to detect  $\text{CoSeCN}^+$  (at  $\lambda = 530$  m $\mu$ ) and  $\text{Co}(\text{SeCN})_4^{2-}$  (at  $\lambda = 630$  m $\mu$ ) complexes. For nickel, according to Ostromyslenskii - Dzhib,  $\text{Ni}(\text{SeCN})_2$ ,  $\text{Ni}(\text{SeCN})_3^-$  and  $\text{Ni}(\text{SeCN})_4^{2-}$  complexes (at  $\lambda = 325$  m $\mu$ ) and  $\text{Ni}(\text{SeCN})_6^{4-}$  complexes (at  $\lambda = 380$  m $\mu$ ) may be detected. The existence of the latter complex was proved by plotting the "formation curve" shown in Fig. 2.

TABLE 1

Dissociation constants	$\text{Ni}(\text{SeCN})_m^{2-m}$	$\text{Co}(\text{SeCN})_m^{2-m}$	Dissociation constants	$\text{Ni}(\text{SeCN})_m^{2-m}$	$\text{Co}(\text{SeCN})_m^{2-m}$
$K_1$	$2.0 \cdot 10^{-3}$	$2.1 \cdot 10^{-4}$	$K_4$	$1.8 \cdot 10^{-7}$	$8.5 \cdot 10^{-6}$
$K_2$	$3.6 \cdot 10^{-5}$	$4.2 \cdot 10^{-5}$	$K_5$	—	$4.6 \cdot 10^{-6}$
$K_3$	$2.0 \cdot 10^{-6}$	$1.8 \cdot 10^{-5}$	$K_6$	—	$2.8 \cdot 10^{-6}$

Therefore in acetone the highest complex for cobalt is  $\text{Co}(\text{SeCN})_4^{2-}$ , and for nickel,  $\text{Ni}(\text{SeCN})_6^{4-}$ . This may be explained by the greater affinity of acetone for the cobalt ion than the nickel ion and its inclusion together with  $\text{SeCN}^-$  addends in the inner sphere. The dissociation constant of  $\text{CoSeCN}^+$  was calculated and was found to be  $1 \cdot 10^{-8}$ . The dissociation constant of  $\text{Co}(\text{SeCN})_4^{2-}$  determined by Komar' [6] was  $7 \cdot 10^{-14}$ . Nickel selenocyanates are less stable in acetone ( $K_1 = 4 \cdot 10^{-4}$ ,  $K_4 = 4.1 \cdot 10^{-11}$ ). The final constants were determined from the "formation curve" (Fig. 2). The investigation of complexing in solution showed that replacement of water by a non-aqueous solvent complicates the composition of the complexes and leads to a marked increase in their stability.

Complexing takes place most readily in acetone. Taking this into account, we carried out a volumetric reaction between  $\text{KSeCN}$  and the corresponding nitrates in a 2 : 1 ratio in an acetone solution. After the precipitate of  $\text{KNO}_3$  had been separated, dioxan was added to the solution. In the case of nickel, blue-green crystals of  $\text{Ni}(\text{SeCN})_2 \cdot 6\text{C}_4\text{H}_8\text{O}_2$ , soluble in acetone and in water, were formed. For cobalt, a light-brown acetone-soluble powder  $\text{Co}(\text{SeCN})_2 \cdot 4\text{C}_4\text{H}_8\text{O}_2$  was obtained in a similar way. An analysis of these salts\* gave the following results.

\* The analytical data of all our synthesized salts are given as the mean values of several determinations.

Found %: Ni 7.30; Se 19.90  $\text{Ni}(\text{SeCN})_2 \cdot 6\text{C}_4\text{H}_8\text{O}_2$ . Calculated %: Ni 7.35; Se 19.80.

Found %: Co 9.80; Se 25.20  $\text{Co}(\text{SeCN})_2 \cdot 4\text{C}_4\text{H}_8\text{O}_2$ . Calculated %: Co 9.51; Se 25.44.

When  $\text{Co}(\text{SeCN})_2 \cdot 4\text{C}_4\text{H}_8\text{O}_2$  was kept under dioxan, rose-colored crystals of  $\text{Co}(\text{SeCN})_2 \cdot 6\text{C}_4\text{H}_8\text{O}_2$  were obtained:

Found %: Co 7.48; Se 19.65  $\text{Co}(\text{SeCN})_2 \cdot 6\text{C}_4\text{H}_8\text{O}_2$ . Calculated %: Co 7.40; Se 19.75.

The salts  $\text{Ni}(\text{SeCN})_2 \cdot 6\text{C}_4\text{H}_8\text{O}_2$  and  $\text{Co}(\text{SeCN})_2 \cdot 6\text{C}_4\text{H}_8\text{O}_2$  rapidly lose dioxan, being converted to dark-brown  $\text{Ni}(\text{SeCN})_2$  or pale-pink  $\text{Co}(\text{SeCN})_2 \cdot 2\text{C}_4\text{H}_8\text{O}_2$  powders, readily soluble in water. We have not yet succeeded in obtaining  $\text{Co}(\text{SeCN})_2$ .

Found %: Ni 21.30; Se 58.42  $\text{Ni}(\text{SeCN})_2$ . Calculated %: Ni 21.80; Se 58.75.

Found %: Co 13.4; Se 35.0  $\text{Co}(\text{SeCN})_2 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ . Calculated %: Co 13.25; Se 35.5

Using anhydrous  $\text{CoCl}_2$  and  $\text{KSeCN}$  (in a 1 : 4 ratio) as the initial salts, we obtained a green powder with the composition  $\text{K}_2\text{Co}(\text{SeCN})_4 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ .

Found %: K 9.7; Co 7.28; Se 38.47  $\text{K}_2\text{Co}(\text{SeCN})_4 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ . Calculated %: K 9.52; Co 7.18; Se 38.47.

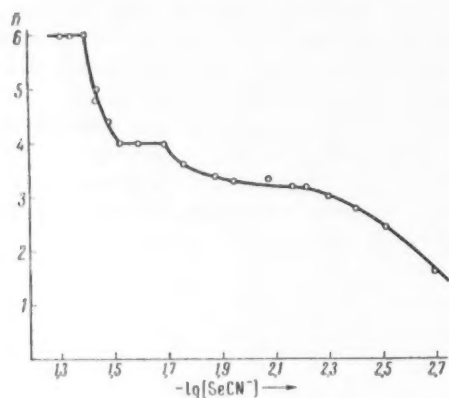


Fig. 2. Formation curve in the system  $\text{Ni}^{2+} - \text{SeCN}^- - \text{CH}_3\text{COCH}_3$  at  $\lambda = 370 \text{ m}\mu$ .

If  $\text{NaSeCN}$  is taken instead of  $\text{KSeCN}$ , lustrous blue plates soluble in acetone and in water are obtained under these conditions. An analysis of the salt obtained indicates that it has the composition  $\text{Na}_2\text{Co}(\text{SeCN})_4 \cdot 7\text{C}_4\text{H}_8\text{O}_2$ .

Found %: Co 5.15; Se 27.75  $\text{Na}_2\text{Co}(\text{SeCN})_4 \cdot 7\text{C}_4\text{H}_8\text{O}_2$ .

Calculated %: Co 5.17; Se 27.70.

We did not succeed in obtaining a salt of similar composition for nickel.

If dioxan ( $\sim 50 \text{ vol } \%$ ) is added to an acetone solution containing  $\text{Co}^{2+}$  and  $\text{SeCN}^-$  in a 1 : 6 ratio, very fine plates are precipitated immediately, being subsequently converted to a blue amorphous mass. The powder obtained is soluble in acetone and is decomposed by water. This salt corresponds to the composition  $\text{K}_3\text{Co}(\text{SeCN})_5 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ .

Found %: K 12.5; Co 6.00; Se 41.20

$\text{K}_3\text{Co}(\text{SeCN})_5 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ .

Calculated %: K 2.11; Co 6.12; Se 41.0.

Recrystallization from an acetone-dioxan mixture leaves the composition of this salt unchanged.

From an acetone solution obtained by mixing  $\text{Ni}(\text{NO}_3)_2$  and  $\text{KSeCN}$  solutions in a 1 : 6 ratio, the salt  $\text{K}_4\text{Ni}(\text{SeCN})_6 \cdot 2\text{CH}_3\text{COCH}_3$  crystallizes after the precipitate of  $\text{KNO}_3$  has been separated. This salt is formed as very fine blue crystals which rapidly decompose in air.

Found %: Ni 6.16; Se 49.63  $\text{K}_4\text{Ni}(\text{SeCN})_6 \cdot 2\text{CH}_3\text{COCH}_3$ . Calculated %: Ni 6.14; Se 49.50.

The data we obtained make it possible to conclude that nickel has a greater tendency to form  $\text{Ni}(\text{SeCN})_6^{4-}$  complexes than cobalt, which readily forms  $\text{Co}(\text{SeCN})_4^{2-}$ . Data on the composition and strength of complex selenocyanates and on the synthesis of the corresponding salts indicate that cobalt and nickel selenocyanates are very similar to the thiocyanates of these metals [11, 12].

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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## THE STRUCTURE OF SABINENE MONOHYDROCHLORIDE

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Semmler [1], who first investigated the hydrochlorination of sabinene, obtained the monochloride with a yield of about 30% and attributed to it the structure of 1-chlorothujane (I). Wallach [2] increased the yield of sabinene monochloride to some extent, and suggested that it had the structure of 1-methylene-4-chloro-4-isopropylcyclohexane (II). It is characteristic that this contradiction has remained in the present literature on terpene chemistry. Thus,

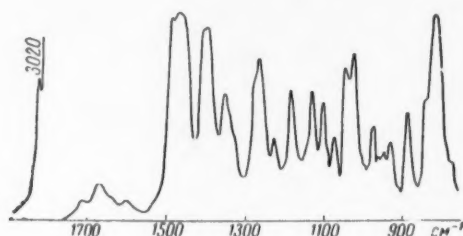
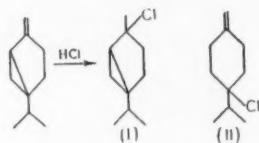


Fig. 1

in his *Traité de chimie organique*, Grignard [3] gives structure II for sabinene monochloride, whereas Simonsen [4] prefers to use the Semmler formula. We established that if the hydrochlorination reaction of sabinene is carried out at  $-30$  to  $-40^\circ$ , an almost quantitative yield of the monohydrochloride is obtained. As regards the structure of this



sabinene derivative, neither the Semmler nor the Wallach formula appears correct to us. The principal argument against structure II is the presence of optical activity for sabinene monochloride. To determine the exact structure of the latter, we recorded the infrared spectra of sabinene and terpinenol-4. The infrared spectrum of sabinene

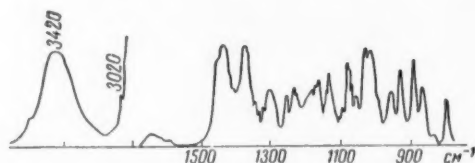


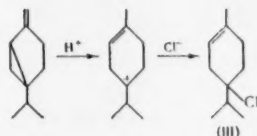
Fig. 2

monohydrochloride (see Fig. 1) contains a weak band at about  $1674\text{ cm}^{-1}$ , characteristic of a double bond. A similar frequency was also found in the infrared spectrum of terpinenol-4 (Fig. 2), whereas sabinene (Fig. 3) has a very strong absorption band at about  $1652\text{ cm}^{-1}$ .



The spectrum of sabinene monochloride and that of terpinenol both contain frequencies of 810 and 3020  $\text{cm}^{-1}$ , characteristic of a trisubstituted double bond. Sabinene absorbs at about 890 and 3075  $\text{cm}^{-1}$  (methylene group) and at about 1028 and 3045  $\text{cm}^{-1}$  (cyclopropane ring).

Therefore sabinene monohydrochloride must be considered to have the structure of 4-chloro-menthene-1 (III), the formation of which may be represented as follows:



#### EXPERIMENTAL

13.6 g of sabinene ( $n_D^{20}$  1.4677;  $d_4^{20}$  0.8441;  $[\alpha]_D^{20} + 102.5^\circ$ ), preliminarily distilled in a current of dry argon over sodium metal, was dissolved in 75 ml of dry petroleum ether and the solution was saturated with a current of thoroughly dried hydrogen chloride. The temperature of the reaction mixture was kept at about  $-30$  to  $-40^\circ$ . After

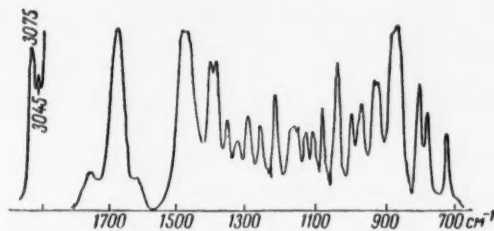


Fig. 3

the usual treatment the product was distilled under vacuum. 16.4 g (95%) of sabinene monohydrochloride was obtained. It had the following characteristics: b. p.  $71-74^\circ/1$  mm,  $n_D^{20}$  1.4837;  $d_4^{20}$  0.9850;  $[\alpha]_D^{20} 7.1^\circ$ .  $C_{11}H_{17}Cl$ . MR Calculated 50.55; Found 50.12.

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THE MICROSTRUCTURE AND SPECTRA OF BENZYLIDENE-  
ANILINE AND AZOBENZENE DERIVATIVES AND THEIR SALTS

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To establish the cause of the deepening of the color of p-dimethylaminoazobenzene (p-Me<sub>2</sub>N-AB) as a result of the addition of H<sup>+</sup>, a comparison with the spectra of p-Me<sub>2</sub>N-benzylideneaniline (p-Me<sub>2</sub>N-BA) and its analogs [2, 3] must be carried out. The correct approach [1, 4, 5] from the aspect of the relation between color and "meso structure" and "meso state" was first made as far back as 1913-1918. It was based on criticism of the quinonoid

TABLE 1. Absorption Spectra of Benzylideneaniline and Azobenzene Derivatives in CHCl<sub>3</sub> with  
C = 10<sup>-3</sup> mole/liter

Expt. no.	Compound, where Ph = p-phenylene or C <sub>6</sub> H <sub>5</sub>	K-band			[HCl] <sup>2</sup> mole/liter
		λ <sub>max</sub>	ε <sub>max</sub>	Δλ	
1	Ph-N=CH-Ph	265	16600	0	
2	Ph-N=CH-Ph-OCH <sub>3</sub>	284	18200	+19	
		(~317)	(~15000)		
3	Ph-N=CH-Ph-OH	285	17250	+20	
		(315)	(14350)		
4	[Ph-N=CH-Ph-O]-K +	360	38400	+95	[KOH] 10 <sup>-1</sup> mole/liter
5	Ph-N=CH-Ph-NMe <sub>2</sub>	356	34100	+91	
6	[Ph-NH+=CH-Ph-OCH <sub>3</sub> ]+Cl-	365	15400	+100	10 <sup>-2</sup>
7	[Ph-NH+=CH-Ph-OH]+Cl-	375	16800	+110	10 <sup>-1</sup>
		(390)	(15900)		
8	[Ph-NH+=CH-Ph-NMe <sub>2</sub> ]+Cl-	436	54200	+171	2 · 10 <sup>-3</sup>
9	Ph-N=N-Ph	317	16350	0	
		(~324)	(~15200)		
10	Ph-N=N-Ph-OCH <sub>3</sub>	350	24400	+33	
11	Ph-N=N-Ph-OH	345	21700	+28	
12	[Ph-N=N-Ph-O]-K +	407	27600	+90	[KOH] · 10 <sup>-1</sup> mole/liter
		(~404)	(~26500)		
13	Ph-N=N-Ph-NMe <sub>2</sub>	407	28600	+90	
14	[Ph-NH+=N-Ph-OCH <sub>3</sub> ]+Cl-	462	28300	+145	10 <sup>-1</sup>
15	[Ph-NH+=N-Ph-OH]+Cl-	465	41200	+148	10 <sup>-1</sup>
16	[Ph-NH+=N-Ph-NMe <sub>2</sub> ]+Cl-	535 <sup>3</sup>	51400 &	+218 <sup>3</sup>	10 <sup>-1</sup>
		525 & 545	51000		

<sup>1</sup> Subordinate bands occurring in the form of curves, indicated by ~.

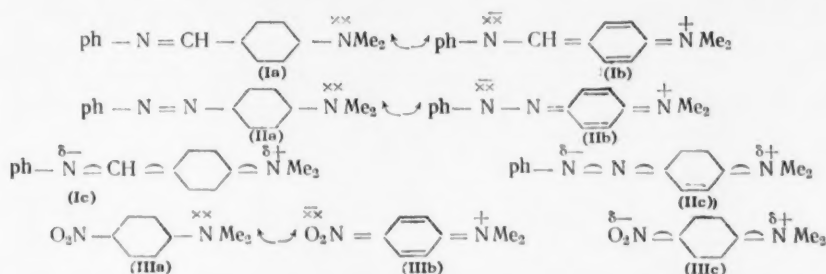
<sup>2</sup> We used HCl solutions in CHCl<sub>3</sub> instead of (CH<sub>3</sub>CO)<sub>2</sub>O [2, 3]. The use of solutions of HCl in EtOH leads to incorrect spectra in the case of azomethines [11].

<sup>3</sup> λ<sub>max</sub> for the half-width of the band. Two peaks indicated below.

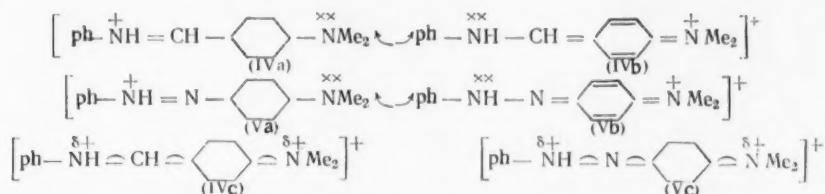
structure, the establishment of the principle of the gradual displacement of the spectrum with a change in structure, and the analogy in the displacements of the spectrum by the action of acid on  $p\text{-Me}_2\text{N}-\text{BA}$ ,  $p\text{-Me}_2\text{N}-\text{AB}$  and by the action of alkali on  $p\text{-O}_2\text{NPhOH}^+$  [2]. The genetics of the spectra were investigated (Table 1).

The electron systems of the azo group or the azomethine group in derivatives of type I, II, IV, and V are chromophoric components, taking part with other chromophoric components in the formation of the combined electron system of the complex chromophore (co-chromophore) [6]. The initial derivatives BA, AB and their HCl salts may be considered as compounds the co-chromophore of which is constructed according to type B-K-A of our classification of chromophoric systems, where K is the conjugated system  $p\text{-C}_6\text{H}_4^-$ ; B is the electrophilic chromophoric components:  $\text{PhN}=\text{CH}$ ,  $\text{PhN}=\text{N}$ ,  $\text{PhNH}=\text{CH}$ ,  $\text{PhNH}=\text{N}$ ,  $\text{NO}_2$ ; A is the electron-donor chromophoric component [6]:  $\text{NMe}_2$ ,  $\text{O}^-$ ,  $\text{OH}$ . The problems consist in the comparison of I, II, IV, and V with the structure and spectra of simpler benzene derivatives of the type B-Ph-A, for example III (Table 1, 4).

The spectrum of bases BA and AB is related to the meso structure. The formulas of the microstructure of Ic and IIc are similar to IIIc. They are a simplified transcription of representations of a displaced structure, resulting from an examination of systems Ia  $\rightsquigarrow$  Ib, IIa  $\rightsquigarrow$  IIb and IIIa  $\rightsquigarrow$  IIIb.\*\*



In accordance with the law of the relation between the bathochromic effect and the degree of electron displacements in the basic state [8], the value of the bathochromic displacement  $\lambda_{\text{max}}$  of the K-band ( $\pi \rightarrow \pi^*$  transition) is greater the more marked the electrophilic character of B and the electron-donor capacity of A. The bathochromic effect resulting from addition of  $\text{H}^+$  to I and II may be explained by the heightening of the electrophilic character of B with replacement of the  $\text{PhN}=\text{CH}$ ,  $\text{PhN}=\text{N}$  groups by  $\text{PhNH}^+=\text{CH}$  and  $\text{PhNH}^+=\text{N}$  groups. The degree of electron displacements expressed by microstructure formulas IVc and Vc may be assessed only by means of a comparison of IVa  $\rightsquigarrow$  IVb and Va  $\rightsquigarrow$  Vb. In Fig. 1 and 2 and Table 1 it may be seen that with an intensification of groups A and B the progressive displacements of the K band do, in fact, resemble very closely the displacements observed for compounds of the type B-Ph-A (Tables 2, 3, and 4).



Systems IVa  $\rightsquigarrow$  IVb and Va  $\rightsquigarrow$  Vb make possible an approach to an explanation of the increase in  $\epsilon$  with transition of the cation charge (Fig. 1 and 2) compared with No. 2, 6, 10, and 14 (Table 1) from the point of view of the approach of the structure to the symmetrical [12] as the result of the presence at the periphery of groups with a similar electron-displacing effect; according to [13] the effect of  $\text{NMe}_2$  (IVb, Vb) is similar to the effect of  $\text{NHPh}$  (IVa, Va).

\* Ph = *p*-phenylene, at the end of the chain = phenyl.

\*\* The symbol  $\rightsquigarrow$ , proposed in [9], is intended to indicate a reduction in the molecular energy, as a result of conjugation and meso structure, compared with the energy values calculated on the basis of possible limiting ("extreme") structural formulas.

TABLE 2. Comparison of the Effects of Bathochromic Displacement of the K-band ( $\Delta\lambda_{\max}^k$ ) in Compounds of the B—\lambda\_{\max} in m $\mu$ )

B	№ 1		№ 2		№ 3		№ 4		№ 5		№ 6
	B for N=CH	NO <sub>2</sub> (14)	$\Delta\lambda$ K no. 1		B for N=N	$\Delta\lambda$ K no. 1	B for NH=CH	$\Delta\lambda$ K no. 1	B for NH=N	$\Delta\lambda$ K no. 1	$\Delta\lambda$ K no. 1
OCH <sub>3</sub>	284	305	+21		350	+66	365	+81	462	+178	+112
OH	285	314	+29		345	+60	375	+90	465	+180	+120
NMe <sub>2</sub>	356	387	+31		407	+51	436	+80	535	+179	+128

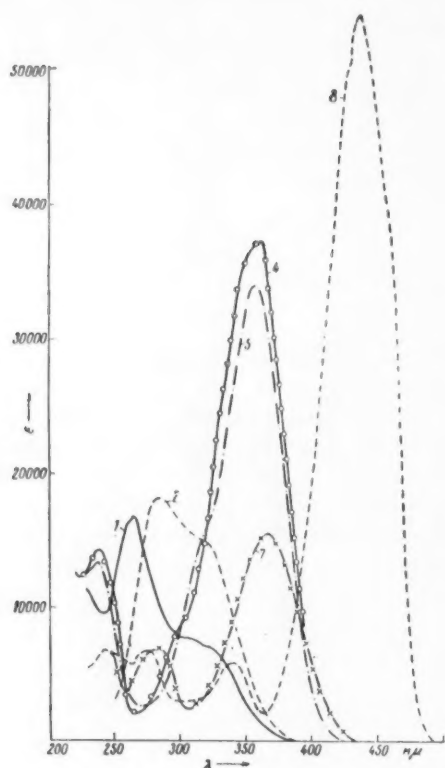


Fig. 1. Absorption spectra of benzylideneaniline; the numbers of the curves correspond to the numbers in Table 1.

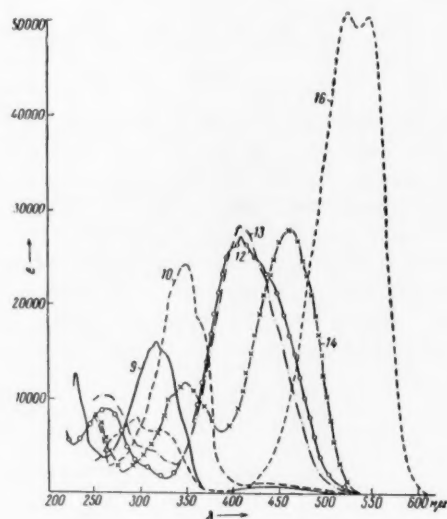


Fig. 2. Absorption spectra of azobenzene derivatives; the numbers of the curves correspond to the numbers in Table 1.

The bathochromic displacement effects with transition of the cation charge as a result of replacement of  $\text{PhN}=\text{CH}$  by the  $\text{PhNH}^+=\text{CH}$  group, were analogous to displacements with an intensification of B without the introduction of a (+) charge and of approximately the same order as with intensification of the donor groups of A. Thus, with replacement of  $\text{PhN}=\text{CH}$  by the  $\text{PhNH}^+=\text{CH}$  group for compounds with different  $\text{A} = \text{OCH}_3, \text{OH}$  and  $\text{NMe}_2$ ,  $\Delta\lambda_{\max}^k$  is 81, 90, and 80 m $\mu$ , while with replacement of the  $\text{PhN}=\text{CH}$  group by an  $\text{PhN}=\text{N}$  group,  $\Delta\lambda_{\max}^k$  is +66, +60, and +51 m $\mu$  (No. 3 and 4, Table 2). With intensification of A: both for compounds with a (+) charge ( $\text{B} : \text{PhNH}^+=\text{N}, \text{PhNH}^+=\text{CH}$ ) and without it ( $\text{B} : \text{PhN}=\text{CH}, \text{NO}_2, \text{PhN}=\text{N}$ ),  $\Delta\lambda_{\max}^k$  is +72, +71, +82, +57, +73 (Table 3, No. 2). Analogously, similar corresponding effects are observed with replacement of  $\text{PhN}=\text{N}$  by a

$\text{PhNH}^+ = \text{N}$  group for compounds with different  $\text{A} = \text{OCH}_3, \text{OH}, \text{NMe}_2$ :  $\Delta\lambda_{\text{max}}^{\text{K}}$  is +112, +120, and +128. The spectra of compounds with  $\text{A} = \text{O}^-$  and with  $\text{A} = \text{NMe}_2$  (No. 4, 5 and 12, 13, Table 1; Fig. 1 and 2) almost coincided:  $\Delta\lambda = +4$  and 0.

TABLE 3. Comparison of the Effects of Bathochromic Displacement of the K-band ( $\Delta\lambda_{\text{max}}^{\text{K}}$ ) in Compounds of the  $\text{B}-\text{C}_6\text{H}_4-\text{A}$  with a Heightening of the Electron-Donor Capacity of the Chromophoric Component A ( $\lambda_{\text{max}}$  in m $\mu$ )

№ 1		№ 2		№ 3	№ 4		№ 5
B	A		$\Delta\lambda$ K no. 1	A OH	A O <sup>-</sup>	$\Delta\lambda$ K No. 3	$\Delta\lambda$ K no. 2
	OCH <sub>3</sub>	NMe <sub>2</sub>					
PhN=CH	284	356	+72	285	360	+75	+4
Ph <sup>+</sup> NH=CH	365	436	+71	—	—	—	—
NO <sub>2</sub> (14)	305	387	+82	314	402.5	+88.5	+15.5
PhN=N	350	407	+57	345	407	+62	0
Ph <sup>+</sup> NH=N	462	535	+73	—	—	—	—

TABLE 4. Parallel Bathochromic Displacement of the K-band in  $\text{B}-\text{C}_6\text{H}_4-\text{A}$  Systems with a Change in Polarity of one of the Chromophoric Components ( $\lambda_{\text{max}}$  in m $\mu$ )

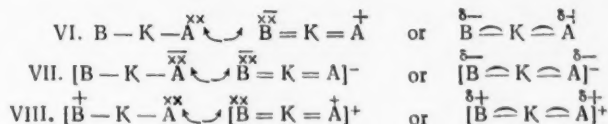
$\text{B} = \text{NO}_2$  is constant and A varies.

	$\text{A} = \text{H} < \text{OCH}_3 < \text{OH} < \text{NH}_2 < \text{NHCH}_3 < \text{NMe}_2 < \text{NEt}_3 < \text{O}^-$								
$\lambda_{\text{max}}$	268	305	314	375(?)	386(?)	387 (14)	390(?)	400(?)	402.5 (14)
$\epsilon_{\text{max}}$	7800	13000	13000	15800	18430	18300	19020	21550	19200

$\text{A} = \text{NMe}_2$  is constant and B varies.

	$\text{B} = \text{COOH} < \text{CH}_2\text{CO} < \text{CHO} < \text{PhN=CH} < \text{NO}_2 < \text{PhN=N} < \text{NO} < \text{PhNH}^+ = \text{CH} < \text{PhNH}^+ = \text{N}$								
$\lambda_{\text{max}}$	308(?)	337(?)	342(?)	356	390(?)	407	423(?)	436	540
$\epsilon_{\text{max}}$	25400	25600	29200	34100	19020	28600	29400	54200	49100

Summing up, we obtain confirmation that chromophores may have an analogous microstructure and an analogous spectral band, irrespective of whether they are anions VII, cations VIII or neutral compounds VI (Table 4) [2, 6, 10], where, for example, K = *p*-phenylene;  $\text{A} = \text{OCH}_3, \text{OH}, \text{NMe}_2, \text{O}^-$ ;  $\text{B} = \text{PhN} = \text{CH}, \text{NO}_2, \text{N} = \text{N}, \text{PhNH}^+ = \text{CH}, \text{NO}, \text{PhNH}^+ = \text{N}$ .



We wish to express our thanks to the management of the Derbenevsk chemical factory for their cooperation in this work.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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# THE REACTION OF 5-ALKOXYOXAZOLES WITH MALEIC ANHYDRIDE

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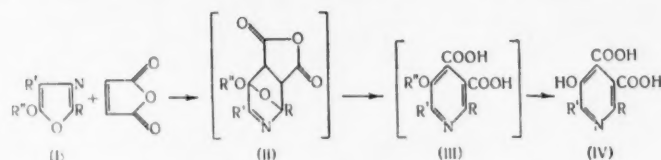
(Presented by Academician B. A. Kazanskii, June 29, 1961)

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It was recently established that alkoxyoxazoles can take part in a diene synthesis reaction with maleic anhydride involving the conjugated system  $C=C-N$ , forming pyridine-3,4-dicarboxylic acids (I). Further investigation of this reaction, which at the same time is a convenient method of obtaining pyridine compounds, will undoubtedly extend the limits of application of the diene synthesis. The present article describes the diene condensation of maleic anhydride and 5-alkoxyoxazoles with different substituents in the 2 and 4 positions.

The reaction was carried out under ordinary diene synthesis conditions, i.e. by heating a benzene solution of oxazole with an excess (2-4 moles) of maleic anhydride in the presence of hydroquinone or pyrogallol. After the



reaction mixture had been boiled with water and the solvent had been evaporated, crystalline reaction products were formed, giving a red or blue-violet color with ferric chloride, characteristic of phenols and  $\beta$ -hydroxypyridines, and having the structure of 5-hydroxypyridine-3,4-dicarboxylic acids.

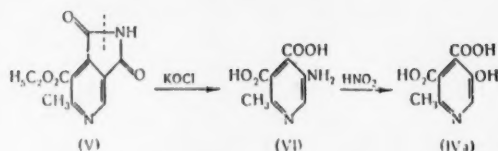
Condensation leads directly to hydroxyacids IV; although very mild reaction conditions and precipitation of the addition products were ensured, we did not succeed in obtaining intermediate compounds II or III. The results of the work are given in Table 1.

TABLE 1. Condensation of 5-Alkoxyoxazoles with Maleic Anhydride

$\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix}$	R	R'	R''	Yield of IV (%)	$\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix}$	R	R'	R''	Yield of IV (%)
a	CH <sub>3</sub>	H	C <sub>2</sub> H <sub>5</sub>	54	g	C <sub>6</sub> H <sub>5</sub> CH=CH	H	C <sub>2</sub> H <sub>5</sub>	0
b	C <sub>2</sub> H <sub>5</sub>	H	C <sub>2</sub> H <sub>5</sub>	47	h	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	36
c	n-C <sub>3</sub> H <sub>7</sub>	H	C <sub>2</sub> H <sub>5</sub>	31.5	i	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	25
d	n-C <sub>3</sub> H <sub>9</sub>	H	C <sub>2</sub> H <sub>5</sub>	42.3	j	n-C <sub>3</sub> H <sub>11</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	15.8
e	n-C <sub>3</sub> H <sub>11</sub>	H	C <sub>2</sub> H <sub>5</sub>	40	k	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	Tarring
f	C <sub>6</sub> H <sub>5</sub>	H	C <sub>2</sub> H <sub>5</sub>	0					

The ultraviolet spectra of hydroxyacids IVa, e, h and j, determined in alkaline solution, are characterized by a well-expressed maximum at 312-315 m $\mu$ . With the exception of IVj, in acid solution the maximum is displaced towards the shortwave region (Fig. 1).

To confirm the structure of the products, one of them - 2-methyl-5-hydroxypyridine-3,4-dicarboxylic acid (IVa) - was obtained by cross synthesis from 6-methyl-5-carbethoxypyridine-3,4-dicarboximide (V) by Hofmann degradation, followed by diazotization of the amino derivative (VI)



Directed degradation of the cyclic imide of the ring is due in this case to the presence of the pyridine nitrogen atom and the carbethoxy group in the 5 position, which leads to weakening of the 4-amide bond [2].

As may be seen from the data of Table 1, lengthening of the carbon chain in the 2 position of oxazole reduces the activity of the heterodiene system. As one passes from  $R = \text{CH}_3$  to  $R = n\text{-C}_8\text{H}_{17}$  (Ia – Ie) the yields of pyridine-hydroxy acids gradually fall from 54 (IVa) to 40% (IVe), and the same effect of the value of the substituent R is ob-

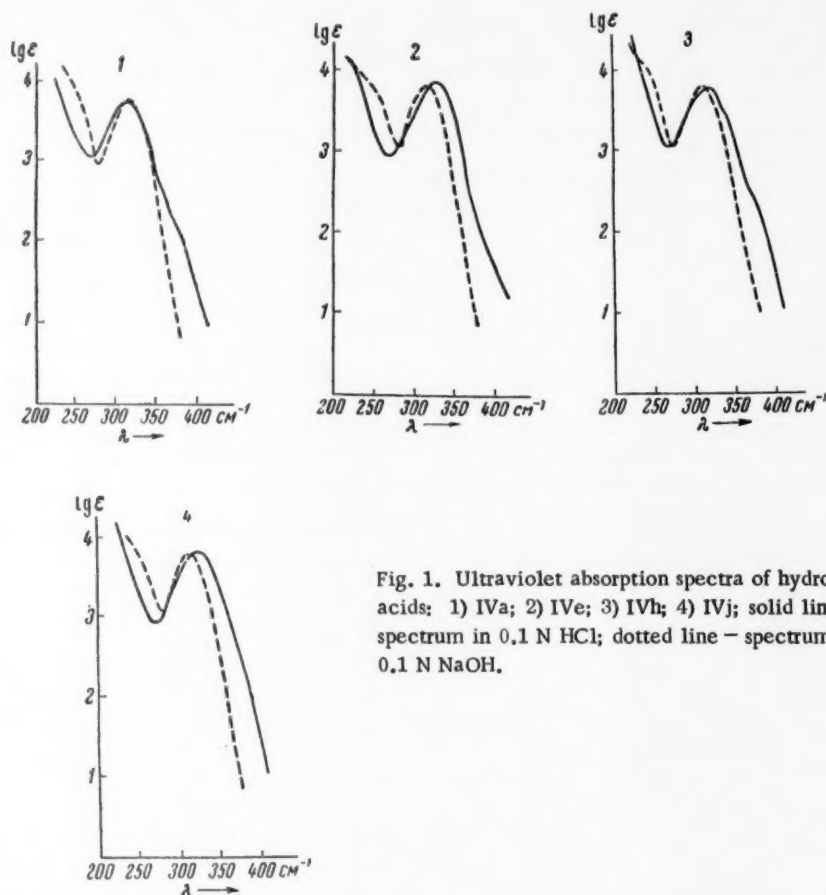


Fig. 1. Ultraviolet absorption spectra of hydroxyacids: 1) IVa; 2) IVe; 3) IVh; 4) IVj; solid line – spectrum in 0.1 N HCl; dotted line – spectrum in 0.1 N NaOH.

served in the series of 2,4-dimethyl-5-alkoxyoxazoles: as a result of condensation of Ij ( $R = n\text{-C}_8\text{H}_{17}$ ), not more than 16% of hydroxyacid IVj was formed, whereas the yields of hydroxy acids IVi and IVh from the lower homologs Ii ( $R = \text{C}_2\text{H}_5$ ) and Ih ( $R = \text{CH}_3$ ) are 25 and 36% respectively.

Variation of the substituent in the 4 position also has a specific effect on the reactivity of alkoxyazoles. A comparison of the results of condensation of Ia – Ie with Ih – Ij makes it possible to assume that the 4-methyl group appreciably deactivates alkoxyazoles in the reaction with maleic anhydride. 2-Alkyl-4-methyl-5-alkoxyoxazoles (Ih – Ij) form addition products with yields approximately 20% less than the corresponding 2-alkyl-5-alkoxyazoles (Ia – Ie), while 2-methyl-4-ethyl-5-ethoxyoxazole (Ik) does not react with maleic anhydride.

In contrast to 2-alkyl-5-alkoxyoxazoles, 2-phenyl-5-ethoxyoxazole (If) and its vinyl analog 2-styryl-5-ethoxyoxazole (Ig) do not undergo condensation with maleic anhydride in benzene or xylene. After continuous heating of the components we obtained only fission products of the oxazole ring: hippuric acid in the case of If, and the ethyl ester of N-cinnamoylglycocoll in the case of Ig.

The 5-hydroxypyridine-3,4-dicarboxylic acids formed during the diene condensation of alkoxyoxazoles are a class of compounds which are very difficult to obtain, but of great importance and suitable for the synthetic production of vitamin B<sub>6</sub> and its analogs. For the synthesis of compounds IV, of which there are presently known only 5-hydroxypyridine-3,4-dicarboxylic acid [3] (IV, R' = R' = H) and 6-methyl-5-hydroxypyridine-3,4-dicarboxylic acid [4-6] (IV, R = H, R' = CH<sub>3</sub>), we developed a considerable number of complex variants based principally on the condensation of cyanacetamide with dicarbonyl compounds by the Hantzsch method [4-7] or on the oxidation of substituted isoquinolines [3, 7]. Our proposed method - condensation of 5-alkoxyoxazoles with maleic anhydride - is the best for the synthesis of 5-hydroxypyridine-3,4-dicarboxylic acids, which makes it possible to vary within wide limits the substituting groups; at the same time, a readily available supply of raw material is ensured.

The authors wish to express their gratitude to Academician B. A. Kazanskii for his interest and help in this work, and to L. A. Kazitsyna for carrying out the spectral investigations.

#### EXPERIMENTAL

##### 2-Methyl-5-hydroxypyridine-3,4-dicarboxylic acid (IVa).

a) 2.35 g of 2-methyl-5-ethoxyoxazole, 7.3 g of maleic anhydride and 0.2 g of hydroquinone in 20 ml of benzene was boiled for 8 hours. After the benzene had been steam distilled the solution was filtered and evaporated on the water bath to about 10 ml. 2.25 g (54%) of IVa was precipitated in the form of white crystals with an m.p. of 239° (with decomp.; from water).  $\lambda_{\max}$  was 310 m,  $\log \epsilon_{\max}$  3.70 (0.1 N HCl);  $\lambda_{\max}$  was 315 m $\mu$ ,  $\log \epsilon_{\max}$  was 3.78 (0.1 N NaOH).

Found %: C 49.23; 49.26; H 3.67; 3.60; N 7.37; 7.47 C<sub>8</sub>H<sub>7</sub>NO<sub>5</sub>.

Calculated %: C 48.74; H 3.58; N 7.11.

b) To 10 g of 2-methyl-5-aminopyridine-3,4-dicarboxylic acid (VI) in 6 ml of water acidified with 1 drop of HCl was added a solution of 0.045 g of NaNO<sub>2</sub> in 2 ml of water. The mixture was heated at 70° until liberation of nitrogen had ceased; it was then treated with urea and the solution was evaporated to 2 ml. The yield of IVa was 0.04 g (40%), the m.p. was 235.5-236.5°. A mixed melt with the hydroxy acid obtained from Ia melted at 235.5-236.5°.

2-Methyl-5-aminopyridine-3,4-dicarboxylic acid (VI). 1.1 g of 6-methyl-5-carbethoxypyridine-3,4-dicarboximide (V) was added in 30 min to 15 ml of a KOCl solution (from 0.39 g of chlorine and 1.7 g of KOH) at 0°. The solution was heated for 1 hour on the water bath, the excess KOCl was decomposed with NaHSO<sub>3</sub>, and was then acidified with a hydrochloric acid mixture to pH 2. After it had been allowed to stand for a week in a cooler, 0.6 g (65%) of VI was precipitated from the solution; the m.p. was 240-240.5° (from water)

Found %: C 46.54; 46.74; H 4.36; 4.38 C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub> · 0.5H<sub>2</sub>O.

Calculated %: C 46.83; H 4.42.

2-Ethyl-5-hydroxypyridine-3,4-dicarboxylic acid (IVb). A mixture of 4.1 g of 2-ethyl-5-ethoxyoxazole, 6.4 g of maleic anhydride and ~ 0.05 g of pyrogallol was boiled for 4 hours in 15 ml of benzene. In a similar way to IVa, 2.9 g (47%) of IVb with an m.p. of 238° (with decomp.) was obtained. After it had been reprecipitated with hydrochloric acid from aqueous ammonia (to pH 2) the m.p. was 240-241° (with decomp.).

Found %: C 51.30; 51.07; H 4.48; 4.58 C<sub>9</sub>H<sub>9</sub>NO<sub>5</sub>.

Calculated %: C 51.19; H 4.29.

2-n-Propyl-5-hydroxypyridine-3,4-dicarboxylic acid (IVc). 1.0 g (31.5%) was obtained in a similar way to IVa from 2.2 g of 2-n-propyl-5-ethoxyoxazole and 4.2 g of maleic anhydride; the m.p. was 216-217° (with decomp.).

Found %: C 53.32; 53.03; H 5.20; 5.32 C<sub>10</sub>H<sub>11</sub>NO<sub>5</sub>.

Calculated %: C 53.29; H 4.88

2-n-Butyl-5-hydroxypyridine-3,4-dicarboxylic acid (IVd). 2.2 g of IVd (42.3%) was obtained in a similar way to IVa from 4.0 g of 2-n-butyl-5-ethoxyoxazole and 6.0 g of maleic anhydride; the m.p. was 198-199°. Found %: N 5.91; 5.86 C<sub>11</sub>H<sub>13</sub>NO<sub>5</sub>. Calculated %: N 5.85.

2-n-Amyl-5-hydroxypyridine-3,4-dicarboxylic acid (IVe). From 3.0 g of 2-n-amyl-5-ethoxyoxazole and 6.0 g of maleic anhydride we obtained 1.65 g (40%) of IVe with an m.p. of 173-174.5°. After recrystallization from water the m.p. was 181-183°.  $\lambda_{\max}$  was 315 m $\mu$ , log  $\epsilon_{\max}$  3.73 (0.1 N HCl);  $\lambda_{\max}$  312 m $\mu$ , log  $\epsilon_{\max}$  3.76 (0.1 N NaOH).

Found %: N 5.31; 5.40 C<sub>12</sub>H<sub>15</sub>NO<sub>5</sub>. Calculated %: N 5.53.

2,6-Dimethyl-5-hydroxypyridine-3,4-dicarboxylic acid (IVh). From 2.6 g of 2,4-dimethyl-5-methoxyoxazole and 8.8 g of maleic anhydride we obtained 1.5 g (36%) of IVh with an m.p. of 269-270° (with decomp.).  $\lambda_{\max}$  was 325 m $\mu$ , log  $\epsilon_{\max}$  3.81 (0.1 N HCl);  $\lambda_{\max}$  315 m $\mu$ , log  $\epsilon_{\max}$  3.84 (0.1 N NaOH).

Found %: C 51.00; 50.82; H 4.53; 4.43; N 6.63; 6.80 C<sub>9</sub>H<sub>9</sub>NO<sub>5</sub>.

Calculated %: C 51.18; H 4.26; N 6.63.

2-Ethyl-6-methyl-5-hydroxypyridine-3,4-dicarboxylic acid (IVi). From 3.0 g of 2-ethyl-4-methyl-5-methoxyoxazole and 6.0 g of maleic anhydride we obtained 1.2 g (25%) of IVi with an m.p. of 217-221° (with decomp.). After reprecipitation from dilute ammonia the m.p. was 233.5-234.5°.

Found %: C 52.78; 52.73; H 4.75; 4.89 C<sub>10</sub>H<sub>11</sub>NO<sub>5</sub>.

Calculated %: C 53.29; H 4.88.

2-n-Amyl-6-methyl-5-hydroxypyridine-3,4-dicarboxylic acid (IVj). From 2.0 g of 2-n-amyl-4-methyl-5-ethoxyoxazole and 4.0 g of maleic anhydride we obtained 0.4 g (15.8%) of IVj with an m.p. of 213-214° (from water).  $\lambda_{\max}$  was 324 m $\mu$ , log  $\epsilon_{\max}$  3.86 (0.1 N HCl);  $\lambda_{\max}$  315 m $\mu$ , log  $\epsilon_{\max}$  3.83 (0.1 N NaOH).

Found %: C 58.80; 58.70; H 6.67; 6.63 C<sub>13</sub>H<sub>17</sub>NO<sub>5</sub>.

Calculated %: C 58.41; H 6.41.

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# THE COMPOSITION OF THE HYDROLYSIS PRODUCTS IN ALUMINUM CHLORIDE SOLUTIONS

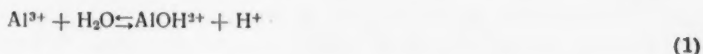
Z. A. Levitskii and V. N. Maksimov

(Presented by Academician I. V. Tananaev July 6, 1961)

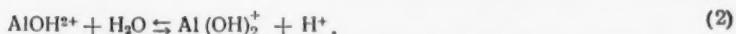
Translated from Doklady Akademii Nauk SSSR, Vol. 141, No. 4,  
pp. 865-868, December, 1961

Original article submitted July 5, 1961

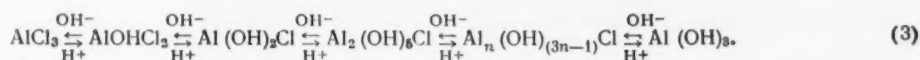
In the literature the hydrolysis of aluminum chloride is considered to be a typical case of step-like hydrolysis of a salt containing a multivalent cation



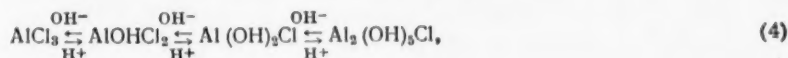
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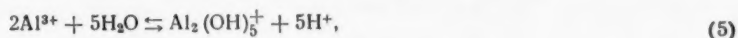
This interpretation has become conventional, and many textbooks mention it as a clear example of step-like hydrolysis [1, 2]. A large number of basic aluminum chlorides have been described. In the process of investigation of these compounds a theory was developed, according to which the system  $\text{AlCl}_3 - \text{Al}(\text{OH})_3$  is a continuous series of basic chlorides, limited by these compounds



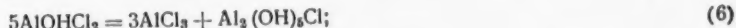
However, an analysis of the large amount of literature data on this problem gives rise to doubts of the correctness of this interpretation. Such information contains a number of experimental data which indicate that at pH 2-6, only the two end compounds  $\text{AlCl}_3$  and  $\text{Al}_2(\text{OH})_5\text{Cl}$  exist, not the series of compounds



In accordance with this, the hydrolysis of aluminum chloride may be described by the reaction



while the basic chloride (of lower basicity) are a mixture



Data which allow a hypothesis to be put forward regarding the hydrolysis of aluminum chloride according to reaction (5) are given below.

1. The existence of a basic salt in the solution is clearly shown by the presence of an inflection (potential discontinuity) on the curve representing the results of the potentiometric titration of the solution of the salt with alkali. At pH 2-6, the potentiometric titration curves of aluminum chloride solutions have only one discontinuity, corresponding to an OH : Al ratio = 2.5, i.e.  $\frac{5}{6}$  of the basic chloride  $\text{Al}_2(\text{OH})_5\text{Cl}$  [3, 4].

2. Curves of the back-titration of hydrolyzed solutions with hydrochloric acid have a similar character. For solution with an OH : Al ratio > 2.5, the inflection of the curve at the point OH : Al = 2.5 is clearly marked, in solutions made alkaline so that OH : Al  $\leq$  2.5 the back-titration curve does not show potential discontinuities [3].

3. During the investigation of solutions with the same Al concentration it was found that with a change in basicity their specific electrical conductivity falls linearly from  $\text{AlCl}_3$  to  $\text{Al}_2(\text{OH})_5\text{Cl}$ . The optical properties of the solutions vary in the same even manner with an increase in the degree of basicity [5].

4. During the investigation of solutions made alkaline so that  $\text{OH} : \text{Al} < 2.5$  a number of properties inexplicable from the aspect of conventional representations of the hydrolysis of aluminum chloride were found.

Thus, in solutions of  $\text{Al}(\text{OH})_2\text{Cl}$  the presence of the cation  $\text{Al}_2(\text{OH})_5^+$  is clearly detected (both from the inflection of the curve of the potentiometric titration with alkali solution [3] and by titration with salts containing a multivalent anion, for example  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ). It is known that during titration of aluminum sulfate with alkali, difficultly soluble basic salts of very varied basicity are formed [6]. Therefore it may be expected that when a sulfate ion (for example an  $\text{Na}_2\text{SO}_4$  solution) is added to a solution of  $\text{Al}(\text{OH})_2\text{Cl}$  a precipitate of  $[\text{Al}(\text{OH})_2]_2\text{SO}_4 - 2/3$  basic sulfate - is formed. However, in actual fact a precipitate of composition  $[\text{Al}_2(\text{OH})_5]_2\text{SO}_4 - 5/6$  basic aluminum sulfate - is always formed [4, 7]. Similar results are observed during titration with salts containing multivalent anions, solutions of basic aluminum chlorides the composition of which varies within the  $\text{OH} : \text{Al}$  ratio range of 1.5-2.5. Experimental proof of the hypothesis of the absence of compounds intermediate between  $\text{AlCl}_3$  and  $\text{Al}_2(\text{OH})_5\text{Cl}$  in the hydrolysis products of aluminum chloride involves a number of difficulties. It is practically impossible to separate the components in an aqueous solution, because they are in equilibrium with each other and when one of them is removed from the system the hydrolytic equilibrium is displaced towards its formation.

However, the problem may be considered from another aspect. If intermediate compounds exist, and hydrolysis in the pH 2-6 range takes place by a step-like mechanism, then, irrespective of the difference in the values of the hydrolysis constants of these compounds, only products of a specific degree of basicity may be contained in partially alkalized solutions. Thus, a solution with  $\text{OH} : \text{Al} > 1$  may contain  $1/3$  basic chloride  $\text{AlOHC}_2$  and more basic compounds (its hydrolysis products); the possibility of the existence of  $\text{AlCl}_3$  in such solutions is excluded. If it is found that  $\text{AlCl}_3$  is contained in preparations of the basic chloride with  $\text{OH} : \text{Al} > 1$ , the conventional theory of step-like hydrolysis is untenable for such a system.

To check this point, we prepared samples with an  $\text{OH} : \text{Al}$  ratio = 0-2.5. The samples were prepared by dissolving very pure aluminum metal in titrated hydrochloric acid by the method described by Denk [7]. Dissolution was intensified by the addition of a catalyst (a drop of mercury). The solutions obtained were evaporated and dried, first in air at room temperature and then in a vacuum desiccator over sulfuric acid and  $\text{P}_2\text{O}_5$  in turn. All the samples obtained were investigated by the x-ray phase analysis method.\* The x-ray diffraction patterns of powders of compounds having the following over-all composition:  $\text{Al}(\text{OH})_{1.06}\text{Cl}_{1.34}$ ;  $\text{Al}(\text{OH})_{1.53}\text{Cl}_{1.47}$ ;  $\text{Al}(\text{OH})_{2.03}\text{Cl}_{0.97}$ , and also  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 3.8\text{H}_2\text{O}$  were determined in the Cu-radiation of a BSV tube.

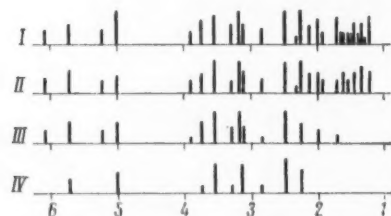


Fig. 1. Line diagram calculated from the x-ray diffraction patterns of aluminum chloride and hydrolyzed products: I)  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ; II)  $\text{Al}(\text{OH})_{1.06}\text{Cl}_{1.34}$ ; III)  $\text{Al}(\text{OH})_{1.53}\text{Cl}_{1.47}$ ; IV)  $\text{Al}(\text{OH})_{2.03}\text{Cl}_{0.97}$ .

As may be seen from the line-diagram obtained from the calculated interplanar spacings (Fig. 1), lines belonging only to aluminum chloride with 6 molecules of water are found on the x-ray diffraction patterns of powders of compounds with a composition intermediate between  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 3.8\text{H}_2\text{O}$ . As a result of the presence of a marked fog, only nine lines could be identified on the photograph of the compound with the composition  $\text{Al}(\text{OH})_{2.03}\text{Cl}_{0.97}$ ; they all coincide with the corresponding lines of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ . This evidently agrees with the data of Kohlshütter [4], who found only weak lines of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  on photographs of samples with the composition  $\text{Al}(\text{OH})_2\text{Cl}$ .

Therefore, x-ray phase analysis showed the presence of considerable amounts of aluminum chloride in preparations with a ratio  $\text{OH} : \text{Al} = 0 - 2$ . This indicates fairly obviously that the conventional interpretation of the hydrolysis process of aluminum

\*X-ray pictures of the samples were taken in the Institute of General and Inorganic Chemistry, Academy of Sciences, USSR, by Yu. N. Mikhailov, to whom the authors wish to express their sincere thanks.

chloride at pH 2-6 by a step-like mechanism is invalid. It is just as obvious that these results still fail to substantiate the proposed hypothesis of the formation of only  $\frac{5}{6}$  basic chloride  $\text{Al}_2(\text{OH})_5\text{Cl}$  during hydrolysis of  $\text{AlCl}_3$  under these conditions. To check this hypothesis we used the method of separation of the components in a non-aqueous medium, where displacement of hydrolytic equilibrium cannot take place as a result of removal of one of the substances.

By way of the solvent we used absolute ethyl alcohol, in which  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  is readily soluble and  $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 3.8\text{H}_2\text{O}$  is practically insoluble. Preliminary experiments showed that substances intermediate in composition between  $\text{AlCl}_3$  and  $\text{Al}_2(\text{OH})_5\text{Cl}$  are not completely soluble in absolute ethanol. A weighed sample of the substance was shaken for 10 minutes with 30 ml of alcohol, the suspension was then filtered through a No. 4 porous glass filter, the precipitate was washed with alcohol on a filter, the alcoholic fraction was removed and the precipitate on the filter was treated with distilled water. The aqueous and alcoholic fractions were then analyzed (gravimetrically) for chlorine and aluminum.

TABLE 1. Separation in Absolute Ethanol

Expt. no.	Initial preparation					Ethanol fraction					Aqueous fraction				
	Cl content		Al content			Cl content		Al content			Cl content		Al content		
	g	g-at. $10^{-3}$	g	g-at. $10^{-3}$	Cl(g-at.) Al(g-at.)	g	g-at. $10^{-3}$	g	g-at. $10^{-3}$	Cl(g-at.) Al(g-at.)	g	g-at. $10^{-3}$	g	g-at. $10^{-3}$	Cl(g-at.) Al(g-at.)
1	0,5012	15,15	0,1362	5,04	3,0	0,5012	15,15	0,1362	5,04	3,0	—	—	—	—	—
2	0,460	12,95	0,1775	6,58	1,94	0,434	12,22	0,1425	5,28	2,31	0,0280	0,79	0,0352	1,32	0,60
3	0,2875	8,10	0,2258	8,36	0,97	0,2993	6,46	0,1500	5,90	1,10	0,062	1,46	0,0667	2,47	0,59
4	1,3260	37,40	1,0410	38,52	0,97	0,7435	20,95	0,2122	7,81	2,68	0,5768	16,26	0,8277	30,64	0,53
5	0,070	1,97	0,1060	3,92	0,5	—	—	—	—	—	0,070	1,97	0,1060	3,92	0,5

The results of the experiments are given in Table 1, from which it may be seen that fairly clear separation is observed in all cases: in the alcoholic fraction the Cl : Al ratio is increased in comparison with the initial preparation, while in the aqueous fraction it is reduced. In this case, if the Cl : Al ratio in the aqueous fraction is close to 0,5 (i.e. the fraction consists of  $\text{Al}_2(\text{OH})_5\text{Cl}$ ) there are a number of difficulties in obtaining a Cl : Al ratio = 3 in the alcoholic fraction. This is the result of contamination of the alcoholic fraction with  $\frac{5}{6}$  basic chloride, caused by part of the precipitate passing through the filter during separation and take-up by the absolute alcohol of water absorbed from the atmosphere and extracted from the hydroxychloride. Elimination of the effect of these factors in experiment No. 4 (see Table 1) made it possible to increase markedly the Cl : Al ratio in the alcoholic fraction (from 1.1 in experiment No. 3 to 2.68 in experiment No. 4).

The experiments carried out showed that the substances intermediate in composition between  $\text{AlCl}_3$  and  $\text{Al}_2(\text{OH})_5\text{Cl}$  are not individual compounds, but mechanical mixtures of aluminum chloride and  $\frac{5}{6}$  basic aluminum chloride. In absolute alcohol these mixtures are divided into fractions consisting of the individual fractions forming the mixture.

Therefore during hydrolysis of aluminum chloride at pH 2-6, not all the theoretically possible basic salts are formed, but only  $\frac{5}{6}$  basic aluminum chloride  $\text{Al}_2(\text{OH})_5\text{Cl}$  (5). The proposed system of hydrolysis of aluminum chloride via  $\frac{5}{6}$  basic chloride (5) makes it possible to explain a number of the above-mentioned phenomena which cannot be interpreted by conventional theories.

It is obvious that if a solution with a basicity  $\text{OH} : \text{Al} < 2.5$  is a mixture of  $\text{AlCl}_3$  and  $\text{Al}_2(\text{OH})_5\text{Cl}$ , the  $\text{Al}_2(\text{OH})_5^+$  cation must be formed in this solution (for example, by the inflection of the potentiometric titration curve). It is also obvious that with addition of multivalent anions (for example  $\text{SO}_4^{2-}$ ) to a hydrolyzed solution of aluminum chloride a precipitate of  $\frac{5}{6}$  basic aluminum sulfate must be formed. In [8] it was shown that  $\frac{5}{6}$  basic aluminum chloride can form products of polymeric structure. For this reason it is possible to consider the so-called "higher" basic chlorides as polymeric varieties of  $\frac{5}{6}$  basic chloride  $\text{Al}_2(\text{OH})_5\text{Cl}$ .

Therefore there is justification for the opinion that during the hydrolysis of aluminum chloride, only one intermediate soluble compound  $\frac{5}{6}$  basic aluminum chloride —  $\text{Al}_2(\text{OH})_5\text{Cl}$  — is formed. The equilibrium of the hydrolysis reactions in this system is expressed as follows:



In conclusion it may be noted that the law shown here (the absence of a number of theoretically possible degrees of hydrolysis in the series  $AlCl_3 - Al(OH)_3$ ) is evidently not a property peculiar to this system alone. Apart from the obvious fact of the hydrolysis of some soluble aluminum salts (for example  $Al(NO_3)_3$ ) [9,3] by this mechanism, we must expect a similar law to be shown for a number of monovalent cations (in particular,  $Ce^{3+}$  and rare-earth metals) [10].

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# MICRODETERMINATION BY GAS CHROMATOGRAPHY OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS

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The presently used methods of analytical determination of carbon and hydrogen in organic compounds by combustion in a stream of oxygen of samples placed into a tube which is either filled with an appropriate catalyst or empty, followed by a gravimetric or volumetric determination of carbon dioxide and water, are time-consuming and require constant attention. Further development of elementary analysis led to combustion followed by determination of the combustion products by gas chromatography; the analysis was expedited and simplified in this manner. The chromatographic methods for the determination of carbon and hydrogen which have been described in the liter-

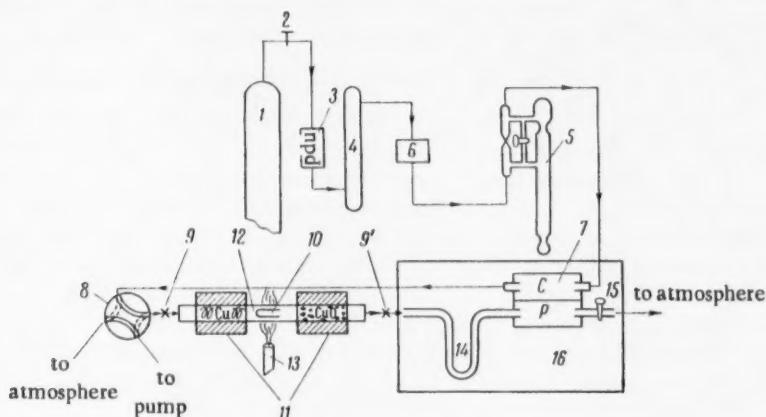


Fig. 1. A schematic representation of the arrangement of the apparatus: 1) source of gas; 2) needle valve; 3) pressure controller (PDU); 4) column for drying filled with magnesium perchlorate; 5) Rheometer; 6) controller of gas flow; 7) detector (C and W-control and working chambers); 8) four-way cock; 9,9') clamps; 10) quartz beaker with sample; 11) electrical furnaces; 12) quartz tube having a length of 35-40 cm. and a diameter of 3-5 mm.; 13) gas burner; 14) chromatographic column having a length of 60 cm. and a diameter of 3 mm; 15) cock; 16) constant temperature chamber.

ature are based on the combustion of organic compounds in an oxygen stream [1] or helium stream [2] in the presence of copper oxide. When this procedure is followed, the reaction products are strongly diluted with the gas in the stream of which combustion is carried out; for this reason the reaction products are frozen out, and the resulting condensate is separated in a column filled with silica gel and analyzed chromatographically. Because water is adsorbed by silica gel in a practically irreversible manner, the water that has formed is first converted into acetylene by reacting it with calcium carbide. This complicates the determination and may result in a partial absorption of  $\text{CO}_2$  by the calcium hydroxide which has formed as a result of the reaction with  $\text{CaC}_2$ . Vogel and Quattrone [3] carried out the



combustion of organic substances in a specially designed bomb filled with oxygen under pressure. The carbon dioxide and water which had formed were separated in a column charged with dodecyl phthalate deposited on diatomaceous earth at 104°.

As distinguished from the methods described, we carried out oxidation of the substance with cupric oxide in an enclosed tube at a residual pressure of 10 mm Hg. Combustion in vacuum had been applied formerly for the determination of carbon, hydrogen, and nitrogen [4]. In the application of the method devised by us the reaction products which formed after combustion were displaced by a helium stream directly into a chromatographic column filled with Inza brick impregnated with tricresyl phosphate in a quantity amounting to 20% of the weight of the carrier [5]. A catharometer was employed as a detector. By using this procedure the shortcomings were eliminated which are inherent in the commonly used methods of combustion, i.e. carrying over the portions of substance which have not been burned and the occurrence of flashes and explosions. Furthermore, we succeeded in surmounting a number of difficulties which arose in connection with the application of chromatographic methods of elementary analysis which had been proposed earlier. The oxidation products were displaced directly by the helium stream from the combustion tube into the chromatographic column, so that it was not necessary to use a dosimeter. Use of tricresyl phosphate as the stationary phase made it possible to conduct separation of carbon dioxide from water at a temperature of 30°. The analysis was carried out under rigidly controlled conditions with respect to the temperature, pressure, and time and did not require constant observation. Consequently, it will be possible to apply the procedure in a completely automatic manner in the future.

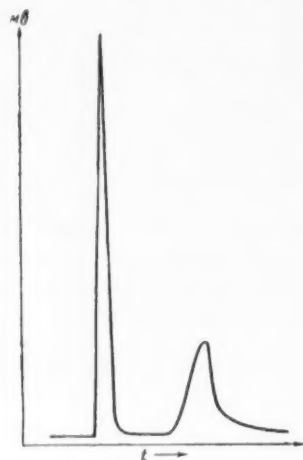


Fig. 2

The determination was carried out as follows (cf. Fig. 1)

The quartz beaker 10 having a length of 3 cm. and a diameter of 2 mm. and containing 2-5 mg. of the substance covered with powdered cupric oxide was placed into tube 12. Helium was passed with a velocity of 60 ml/min through the equipment until air was completely displaced. This was recorded on the tape of an EPP - 09 automatic recorder. Then cock 15 was opened followed by opening of the clamp 9' and tube 12 was connected by means of cock 8 with a vacuum pump or water ray pump. After tube 12 had been evacuated until the residual pressure in it amounted to 10 mm Hg, while the furnaces 11 were brought to a temperature of 700°, clamp 9 was closed. Then the sample was heated for 8-10 min. by means of the flame of gas burner 13 and clamp 9 was opened, whereupon helium was immediately introduced into the tube. Following this clamp 9' and cock 15 were opened in succession and the combustion products that had formed were transferred by means of the helium stream into chromatographic column 14 with a length of 60 cm and a diameter of 3 mm. Because the carbon

TABLE 1

Name of substance	C, %		Difference	H, %		Difference
	found	calc.		found	calc.	
Benzoic Acid, $C_7H_6O_2$	69.23	68.84	+0.39	4.66	4.95	-0.29
	69.18		+0.34			-0.20
Acenaphthene, $C_{12}H_{10}$	93.50	93.46	+0.04	4.75	6.54	-0.17
	93.62		+0.16	6.37		-0.11
2-ethylanthraquinone, $C_{16}H_{12}O_2$	81.26	81.34	-0.08	6.43	5.12	-0.12
	81.14		-0.20	5.00		-0.11
2-phenyl-3-carbethoxy-5-methoxy-6-methylbenzofurane, $C_{15}H_{18}O_4$	73.20	73.53	-0.33	5.01	5.84	0.0
	73.68		+0.15	5.84		+0.07
Ascorbic acid, $C_6H_8O_6$	40.64	40.92	-0.28	5.91	4.58	+0.21
	41.24		+0.32	4.79		-0.26
				4.32		

dioxide was removed rapidly from the column and the peak which formed did not fit onto the chromatographic recording, the velocity at which helium was introduced was reduced to 20 ml/min and the scale was enlarged by a factor of 5. After the CO<sub>2</sub> had been displaced, the rate of flow of helium was increased to 60 ml/min and the automatic recorder was switched over to a more sensitive scale (10 mv). These conditions were necessary in order to bring about the appearance of the water peak on the chromatographic curve. Fig. 2 shows a chromatographic curve which was obtained on combustion of salicylic acid.

Calculation of the content of carbon and hydrogen was carried out by comparing the areas under the CO<sub>2</sub> and H<sub>2</sub>O peaks with values derived from an absolute scale curve that had been constructed earlier on the basis of peak areas obtained by the combustion of salicylic acid. Measurement of the area of the CO<sub>2</sub> peak was carried out by multiplying the height of the peak by the width of the band. The area of the non-symmetric water peak was measured planimetrically. The completeness of the combustion of salicylic acid, on the basis of which the standard curve had been constructed, was checked in the following manner. After combustion of the sample under the conditions described above, when the chromatographic curve had been recorded, the tube was heated for a second time. As a result of the second heating, a straight line was recorded on the tape of the automatic recording instrument, which indicated that additional combustion products were absent.

By applying the method described, organic substances were analyzed for their C, H, and O content (see Table 1).

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## A NEW PRINCIPLE TO BE APPLIED IN THE PREPARATION OF IODONIUM COMPOUNDS

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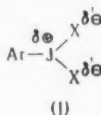
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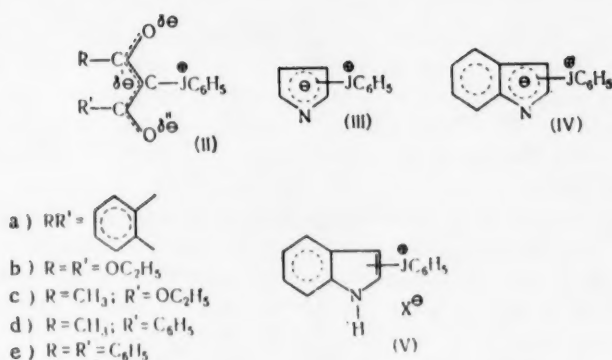
At present several methods for the preparation of diaryliodonium salts are known. The classical method of Hartmann and Meyer [1] involves the use of aryliodoso compounds and aryliodo compounds, which are not always readily accessible. In Willgerodt's method [2] aryliodosochlorides and aryl mercury compounds are used. Freidlina and Nesmeyanov [3] demonstrated that organo-tin compounds can be used instead of organo-mercury compounds. Aryliodination of aromatic hydrocarbons with aryliodoso compounds or inorganic compounds of polyvalent iodine in the presence of concentrated sulfuric acid [4, 5] or trifluoroacetic acid [6] is widely used. It was shown recently that aryliodination with aryliodoso compounds can be carried out very easily in the case of substances which contain mobile hydrogen atoms; namely, nitrophenols [7] or  $\beta$ -dicarbonyl compounds [8, 9].

The experimental data which are available make it possible to conclude with sufficient certainty that the reaction of aryliodination is one involving electrophilic substitution at an aromatic or other nucleophilic carbon atom [10]. The molecule of the aryliodoso compound (I) with strongly polarized bonds functions as the electrophilic particle.



One may assume that the lower the basicity of the anion  $\text{X}^-$  (i.e. the greater the acidity of  $\text{HX}$ ), the greater will be the extent to which the electrophilic quality of the iodoso particle I increases. In this manner one can explain the necessity of having strong acids present in order that the aryliodination of aromatic hydrocarbons may take place. The electrophilic quality of iodoso compounds, although it is reduced in magnitude, must be preserved in alkali solutions as well, i.e. in the case when  $\text{X} = \text{OH}$  in I. This is actually confirmed by the very first reaction in the preparation of iodonium salts from iodosoaryls and iodoaryls in the presence of silver oxide [1]. One may assume that in the presence of a sufficiently active nucleophilic component aryliodination will take place in an alkaline solution. This was recently confirmed experimentally by reacting iodosobenzene with 5,5-dimethylcyclohexanedione-1,3 in an alkaline solution [8].

It has now been established that the reaction between iodoso compounds and nucleophilic components in alkaline solution can be applied quite generally and that aryliodoniumbetaines form as products of this reaction. We investigated the capacity of phenyliodosoacetate (I,  $\text{Ar} = \text{C}_6\text{H}_5$ ;  $\text{X} = \text{OOCCH}_3$ ) to react in the presence of caustic alkali or alcoholate at temperatures from minus  $5^\circ$  to plus  $5^\circ$  in methyl alcohol solutions with a number of substances capable of forming nucleophilic anions, i.e. indandione 1, 3 [10], malonic ester, acetoacetic ester, acetylacetone, benzoylacetone, dibenzoylmethane, phenol, resorcinol, cyclopentadiene, pyrrole, indole, phenylnitromethane, and cyclohexanone. All of these substances reacted. In the cases of phenol, resorcinol, and cyclopentadiene dark products formed as a result of oxidative decomposition. All  $\beta$ -dicarbonyl compounds investigated, with the exception of acetylacetone, formed crystalline phenyliodonium enolate - betaines of low stability [11]. In the case of acetylacetone there was formation of a noncrystallizing oil of low stability which exhibited the properties of enolate-betaines and which could not be isolated in a pure state.



Similarly, pyrrole and indole formed phenyliodoniumbetaines which were yellow and which had the supposed structures III and IV. In the cases of cyclohexanone and phenylnitromethane, betaines of this type could not be isolated. Only decomposition products (iodobenzene and oily substances which could not be identified) were found.

The reaction which took place can be formulated as a regular electrophilic substitution taking place by the way of an intermediate complex:

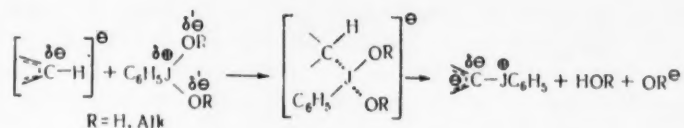


TABLE 1. Phenyliodonium Betaines

Substance	Color and decomposition point on rapid heating	Found %		Calculated %		Infrared absorption spectra (suspensions in paraffin oil)	Intensity (chloroform solutions)
		I	N	formula	I	N	
IIa	Yellow needles, 107-109° (did not crystallize)	36.84	—	$C_{15}H_9O_2I$	36.45	—	1595( $\epsilon = 630$ ) 1630( $\epsilon = 600$ )
IIb	White crystals, 89-90°	34.80	—	$C_{13}H_{15}O_4I$	35.04	—	1560(inflection) 1631( $\epsilon = 350$ )
IIc	Yellowish crystals, 84-85°	34.82 37.95 38.11	—	$C_{12}H_{13}O_3I$	38.21	—	1654( $\epsilon = 350$ ) 1538(60); 1630(53) 1568(88) 1650(87)
IId	Yellow needles, 88-89° (explosive decomp.)	34.69 34.56	—	$C_{16}H_{13}O_2I$	34.85	—	1482(85); 1580(64) 1536( $\epsilon = 800$ )
IIe	Yellow needles, 92-93° (explosive decomp.)	28.86 30.16	—	$C_{21}H_{15}O_2I$	29.77	—	1465-1477(98); 1569 (39) 1524-1530 ( $\epsilon = 800$ ) 1568(inflect.) 1602(inflect.)
III	Yellow crystals, 75° (explosion)		5.33	$C_{10}H_8NI$	47.21	5.20	
IV	Yellow crystals, 95° (explosive decomp.)		3.88 4.13 4.68	$C_{14}H_{10}NI$	39.76	4.39	
V	White needles, 84° (explosive decomp.)	31.02 30.71 32.47		$C_{14}H_{11}NBrI$	31.72	3.50	

The phenyliodoniumbetaines which had been isolated were substances of low stability which decomposed rapidly during recrystallization and storage. The decomposition point depended greatly on the velocity with which the substance was heated. The presence of acids was found to speed up decomposition. The indole betaine IV formed unstable iodonium salts of the type V. When V was subjected to the action of an alkali, IV formed again. Analogous iodonium salts of pyrrole could not be isolated in a pure and dry state. When the presumable bromide was dried, explosive decomposition took place.

The structure of the phenyliodoniumenolate betaine (II) was partially confirmed by the infrared absorption spectra, in which valency vibrations corresponding to a normal carbonyl group were not observed. One did observe strong lowering of the frequency, which indicated that there was formation of systems with a fractional number of bonds, i. e. conjugated enolate anions [9, 11, 12]. The correctness of the assumed structure was also confirmed by a low stability towards acids, the formation of iodobenzene on decomposition, and the strong yellow coloration of chloroform solutions [8, 9, 12]. The structure of the pyrrole and indole iodonium derivatives was confirmed in part by their chemical behavior and their low stability. Whether the substitution took place in the  $\alpha$  or  $\beta$  position has not yet been established.

It has thus been found that aryliodoso compounds react with nucleophilic particles in alkaline solution, forming readily iodonium betaines. The iodonium betaines are unstable substances which on the other hand are highly reactive and thus presumably can be used for various further transformations. Obviously, the reaction in question can be extended to many other compounds which are capable of furnishing a strong nucleophilic center and of forming betaines after substitution.

Some of the experimental data obtained are listed in Table 1. The iodine was determined by Schoeniger's method [13]. In the case of substances III and IV it was not possible to obtain satisfactory results, because on heating explosive decomposition took place and a part of the decomposition products volatilized without burning. The infrared spectra were taken on IKS-12 and IKS-14 instruments after the substances had been suspended in paraffin oil or dissolved in chloroform.

We express our thanks to D. Kreitsberg and A. Zeltyn' for the rapidly conducted microanalytical determinations and to E. Zarinyu for the infrared absorption spectra which were taken.

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## SYNTHESIS AND SPECTRA OF DEUTERONITROFORM

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(Presented by Academician A. V. Topchiev, May 5, 1961)

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Trinitromethane (nitroform), being a strong acid, reacts readily with conjugated unsaturated compounds, i.e. aldehydes [1], ketones [1, 2], acids and their esters [1], nitriles [1], and vinyl ethers [3]. After the reaction of nitroform with 2-nitroalkenes [4] one can separate quantitatively aci-1,1,1,3-tetranitroalkanes.

TABLE 1

Compound	M. p., °C	B. p., °C/mm	$n_D^{30}$	$d_4^{30}$
$(O_2N)_3CH$	26,5 [3]	48/15	1,4448	1,6136
$(O_2N)_3CD$	27,4—27,6	43/10	1,4430	1,6173

In order to investigate in detail the addition reactions of nitroform and also the tautomeric transformations of aci-nitroalkanes, it seemed advantageous to us to apply the method of tracer atoms. With this end in view, we synthesized deuterionitroform by reacting dry deuterium chloride with the potassium salt of trinitromethane suspended in methylene chloride:  $(O_2N)_3CK + DCl \rightarrow (O_2N)_3CD + KCl$ .

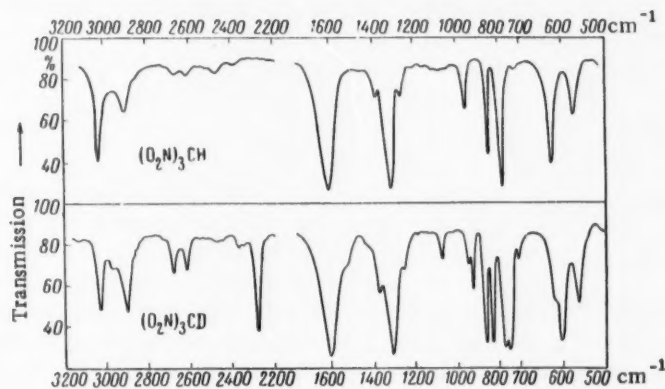


Fig. 1. Infrared absorption spectra of nitroform and deuterionitroform.

The deuterionitroform prepared in this manner consisted of colorless hygroscopic crystals having a melting point of 27.4-27.6°. The isotope content of the deuterated product was determined by mass spectrography and found to be 98.5%. As far as its physical properties are concerned, deuterionitroform differs but little from ordinary nitroform. In Table 1 the physical properties of deuterionitroform are compared with those of nitroform prepared similarly by reacting the potassium salt of trinitromethane with dry hydrogen chloride.

The Raman spectra (on a ISP-51 spectrograph) and the infrared spectra (on a UR-10 spectrometer) of both deuterionitroform and ordinary nitroform were taken. The results obtained are presented in Table 2 and Fig. 1.

As can be seen from the data on the spectra, both compounds have the same band at 830-833  $cm^{-1}$ , which is characteristic for valency vibrations of the C-N bond, and also absorption bands at 1600-1608 and 1305-1310  $cm^{-1}$ , which are associated respectively with the antisymmetric and symmetric valency vibrations of the trinitromethyl group.

TABLE 2

(O <sub>2</sub> N) <sub>3</sub> CH		(O <sub>2</sub> N) <sub>3</sub> CD		(O <sub>2</sub> N) <sub>3</sub> CH		(O <sub>2</sub> N) <sub>3</sub> CD	
Raman spectrum, cm <sup>-1</sup>	Infrared spectrum, cm <sup>-1</sup>	Raman spectrum, cm <sup>-1</sup>	Infrared spectrum, cm <sup>-1</sup>	Raman spectrum, cm <sup>-1</sup>	Infrared spectrum, cm <sup>-1</sup>	Raman spectrum, cm <sup>-1</sup>	Infrared spectrum, cm <sup>-1</sup>
213(1)		202(1)		1305(6)	1305	1310(4 broad)	1310
376(5)		374(3)		1370(4)	1370	1374(3 broad)	1374
401(3 broad)		391(2 broad)		1408(1)		1408(0)	
415(3 broad)		408(3 broad)		1608(4 broad)	1600	1602(2 broad)	1605
570(1)	570		566	1623(4 broad)		1622(2 broad)	
		602(2)	605			2266(1)	2270
625(2)	625				2612		2612
	708		708		2670		2670
		750(6 broad)	750	2837(1)			
777(2)	773		770		2902		2902
833(4)	833	833(3)	830			2972(0)	
		868(1)	865		3033		3033
		926(4)	925	3042(3)			
948(10)	944		945				
		1062(2 broad)	1065				
1251(3 broad)	1251						

Furthermore, the spectra of deuterionitroform exhibited an intense band at 2266-2270 cm<sup>-1</sup>, which corresponds to valency vibrations of the carbon-deuterium (C-D) bond. One may note that the spectrometric data obtained are of considerable value for the calculation and detailed correlation of the frequencies of vibrations of the trinitromethyl group.

#### EXPERIMENTAL

**Preparation of deuterionitroform.** In a four-neck flask equipped with an agitator having a seal, a thermometer, a reflux condenser with a calcium chloride tube, and an inlet for bubbling gas through the liquid, 47.8 g (0.5 moles) of freshly prepared dry potassium salt of trinitromethane [5] were suspended in 250 ml of dry methylene chloride. Into the mixture which was being agitated, dry deuterium chloride was bubbled at room temperature until disappearance of the yellow coloration. The deuterium chloride was prepared according to Brown and Groot [6] from 4 ml of heavy water (containing 99.97% of D<sub>2</sub>O) and 100 g of benzoyl chloride. Because of the hygroscopicity of deuterionitroform all subsequent operations were carried out in a box in a dry nitrogen atmosphere. By subjecting the reaction mixture to the pressure of dry nitrogen, this mixture was filtered through a glass filter into a round-bottom 0.5 l flask. The precipitate was washed with 50 ml of dry methylene chloride. The solvent was removed by evaporation in a vacuum of 15-20 mm on a warm (30-35°) bath, whereupon the residue was distilled from a Favorskii flask. The deuterionitroform fraction with a boiling point of 43° at 10 mm was collected. This fraction consisted of a colorless liquid which solidified into a crystalline mass on being seeded or frozen out. The yield was 30.4 gr. (80% of theory), m.p. 27.4-27.6° (on crystallization from hexane under freezing),  $n_D^{20}$  1.4430 and  $d_4^{30}$  1.6173.

Found %: C 8.17; 8.21; D 1.31; 1.66; N 27.83; 27.95 CN<sub>3</sub>O<sub>3</sub>D.

Calculated %: C 7.90; D 1.32; N 27.65.

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# ACTIVITIES, HEATS OF MIXING, AND ENTROPIES OF MIXING IN SOLID $\text{NiFe}_2\text{O}_4 - \text{Fe}_3\text{O}_4$ SOLUTIONS

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The equilibrium conditions pertaining to  $\text{NiFe}_2\text{O}_4 - \text{Fe}_3\text{O}_4$  solid solutions following reduction of nickel ferrite with hydrogen under equilibrium conditions at different temperatures were investigated. A weighed-in quantity of  $\text{NiFe}_2\text{O}_4$  was placed in an enclosed vacuum apparatus through which an  $\text{H}_2 + \text{H}_2\text{O}$  mixture was circulated. The pressure of the water corresponded to saturated vapor tension at  $0^\circ\text{C}$ . Equilibrium was reached from both sides, that

of reduction and that of oxidation, and the mean value of hydrogen pressure was assumed to be equal to the equilibrium  $P_{\text{H}_2}$ . The data in question are listed in Table 1. On the basis of the equilibrium hydrogen pressures, the equilibrium constants of the reaction of reduction were calculated according to the expression

$$K_p = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}.$$

An x-ray diffraction analysis of the reaction products indicated that after the reduction of  $\text{NiFe}_2\text{O}_4$  metallic Ni with an admixture of Fe had separated out and the solid solution  $\text{NiFe}_2\text{O}_4 - \text{Fe}_3\text{O}_4$  had formed. On the basis of changes in the dimensions of the crystal lattice of the metallic phase and data reported in [1], the molar fractions of  $\text{NiFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  in the solid solutions were calculated (see Table 1). Knowledge of the molar fraction  $N_f$  of ferrite and the molar fraction  $N_m$  of magnetite as well as of the equilibrium constants made it possible to calculate the ferrite activities  $\alpha_f$  and magnetite activities  $\alpha_m$  in solutions of varying composition. The condition corresponding to ferrite reduced to the extent of 0.1% was taken as a standard. The activity of

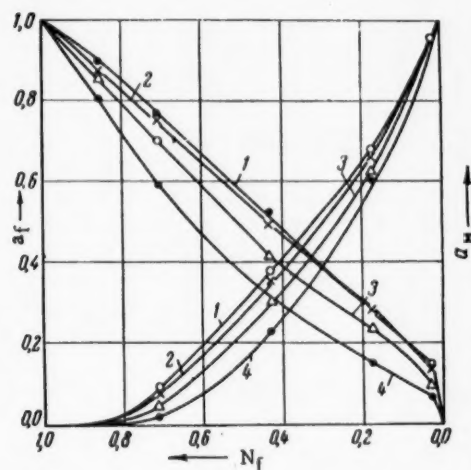


Fig. 1. Changes in the activities of ferrite and magnetite in the system  $\text{NiFe}_2\text{O}_4 - \text{Fe}_3\text{O}_4$  in relation to the composition: 1)  $900^\circ$ ; 2)  $800^\circ$ ; 3)  $700^\circ$ ; 4)  $600^\circ$ .

ferrite was determined as  $\alpha_f = \frac{K_{p1}}{K_{p0}}$ , while the coefficient of activity was calculated according to the equation

$$\alpha_f = \gamma_f N_f.$$

The activities of  $\text{Fe}_3\text{O}_4$  were determined by graphic integration of the Gibbs-Duhem equation:

$$\ln a_f = - \int \frac{1 - N_f}{N_f} d \ln a_m.$$

The coefficient of the activity of  $\text{Fe}_3\text{O}_4$  was determined as  $\gamma_m = \frac{\alpha_m}{1 - N_f}$ . The data obtained in this manner are listed in Table 1. The changes of activity are shown in Figure 1.

The partial free energies of mixing were calculated according to the formula  $\Delta \bar{F}_i = RT \ln \alpha_i$ , whereas the total energy of mixing was determined from the expression  $\Delta F_{\text{mix}} = \Delta \bar{F}_f \cdot N_f + \Delta \bar{F}_m \cdot N_m$ .

TABLE 1. Activities of Constituents of Solid Solutions in the  $\text{NiFe}_2\text{O}_4 - \text{Fe}_3\text{O}_4$  System

$N_f$	800° C						700° C						600° C							
	$P_{H_2}$ mm pt.ct.			$P_{H_2}$ mm pt.ct.			$P_{H_2}$ mm pt.ct.			$P_{H_2}$ mm pt.ct.			$P_{H_2}$ mm pt.ct.			$P_{H_2}$ mm pt.ct.				
	$c_f$	$a_m$	$\gamma_f$	$\gamma_m$	$a_f$	$a_m$	$\gamma_f$	$\gamma_m$	$a_f$	$a_m$	$\gamma_f$	$\gamma_m$	$a_f$	$a_m$	$\gamma_f$	$\gamma_m$	$a_f$	$a_m$	$\gamma_f$	$\gamma_m$
0,160	0,031	1,000	0,000	0,000	1,000	0,041	1,000	0,000	0,046	1,000	0,000	0,000	0,048	1,000	0,000	1,000	0,000	0,000	0,000	0,000
0,850	0,033	0,903	0,007	1,055	0,050	0,046	0,892	0,006	1,042	0,040	0,052	0,883	0,002	1,030	0,017	0,058	0,816	0,0005	0,952	0,003
0,717	0,040	0,771	0,090	1,078	0,318	0,054	0,764	0,082	1,068	0,290	0,064	0,712	0,053	0,993	0,187	0,081	0,597	0,026	0,835	0,092
0,435	0,057	0,530	0,373	1,220	0,661	0,081	0,505	0,360	1,160	0,638	0,109	0,420	0,309	0,965	0,547	0,191	0,305	0,244	0,703	0,432
0,179	0,107	0,281	0,665	1,570	0,810	0,142	0,289	0,665	1,620	0,810	0,190	0,241	0,636	1,345	0,775	0,320	0,150	0,613	0,839	0,748
0,020	0,189	0,159	0,953	7,940	0,970	0,295	0,138	0,953	6,900	0,970	0,444	0,103	0,946	5,150	0,965	0,610	0,078	0,937	3,910	0,955

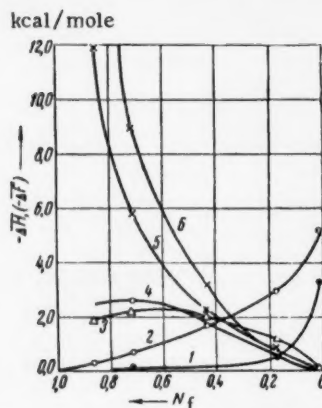


Fig. 2. Variation of the partial free energies and enthalpies of mixing for solid solutions in the system  $\text{NiFe}_2\text{O}_4 - \text{Fe}_3\text{O}_4$ : 1)  $\Delta H_f$ ; 2)  $\Delta F_f$ ; 3)  $\Delta F_n$ ; 4)  $\Delta H_n$ ; 5)  $\Delta F_m$ ; 6)  $\Delta H_m$ .

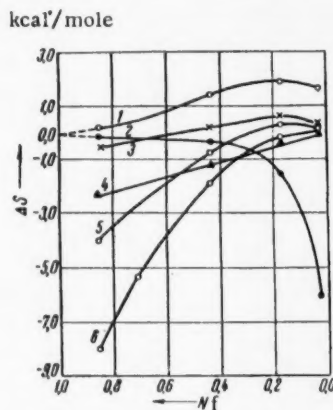


Fig. 3. Variation of entropies of mixing for solid solutions of the system  $\text{NiFe}_2\text{O}_4 - \text{Fe}_3\text{O}_4$  in relation to the composition: 1)  $\Delta S_f$ ; 2)  $\Delta S_{f \text{ excess}}$ ; 3)  $\Delta S_n$ ; 4)  $\Delta S_{n \text{ excess}}$ ; 5)  $\Delta S_m$ ; 6)  $\Delta S_{m \text{ excess}}$ .

In view of the fact that the temperature dependence of these functions is very weakly pronounced, their values were averaged out. The data in questions are shown in Figure 2.

On applying to the solid solutions of ferrites the theory of regular solutions [2], we found the partial enthalpies of mixing from the formula

$$4,575 \lg \gamma_i = \overline{\Delta H_i} \frac{1}{T} + \text{const},$$

and the total enthalpies of mixing from the formula

$$\Delta H_{n_i} = \overline{\Delta H}_i \cdot N_{f_i} + \overline{\Delta H}_m \cdot N_{m_i}.$$

The partial entropies were calculated by a method similar to that applied in [3], from the expression

$$\overline{\Delta S}_i = \frac{\overline{\Delta H}_i - \overline{\Delta F}_i}{T},$$

while the total entropies were calculated according to the formula

$$\Delta S_{n_i} = \overline{\Delta S}_i \cdot N_{f_i} + \overline{\Delta S}_m \cdot N_{m_i}.$$

Because the entropies vary with the temperature to only a very small extent, mean values of the entropies were calculated. These values are shown in Figure 3.

The excess entropies of mixing were calculated by a method similar to that used in [4], from the expression

$$\Delta S_{i_{\text{excess}}} = \overline{\Delta S}_i - \Delta S_{i_{\text{ideal}}}.$$

It follows from the theory of regular solutions [5] that  $\Delta S_{i_{\text{ideal}}} = -R \ln N_i$ . Excess entropies of mixing are usually related in a complex manner to the composition. For the compositions investigated at 900°, the relationship involved could be represented by the curves shown in Figure 3. The excess entropies characterize the degree of orderliness of solid solutions. In the first approximation one may say that the degree of orderliness in the system  $\text{NiFe}_2\text{O}_4 - \text{Fe}_3\text{O}_4$  changes according to curve 2 for  $\text{NiFe}_2\text{O}_4$ , according to curve 6 for  $\text{Fe}_3\text{O}_4$ , and according to curve 4 for the solid solution as a whole.

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# CALCIUM GERMANATES AND THEIR PROPERTIES

S. M. Royak and I. A. Prokhvatilova

(Presented by Academician S. I. Vol'fkovich, July 15, 1961)

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Original article submitted July 13, 1961

The periodic variation of bonding properties exhibited by chemical compounds of the type of calcium silicates, which was discovered by V. A. Kind and V. A. Churavlev [1], was also found to exist in the case of synthetic dicalcium germanate prepared by sintering at 1250°. Dicalcium germanate was also prepared by Ludekens, who applied sintering at 1100° [4].

It appeared of interest to subject to more detailed investigation dicalcium germanate and to establish whether or not tricalcium germanate is formed by analogy with the most important clinker mineral, i.e. tricalcium silicate.

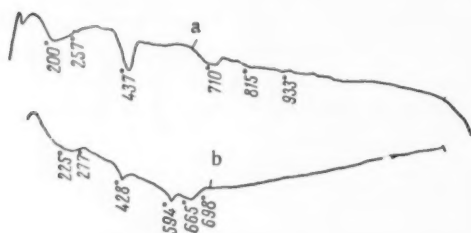


Fig. 1. Differential curves of the heating of dicalcium germanate (a) and  $\beta$ -dicalcium silicate (b).

To synthesize calcium germanates, chemically pure dried calcium carbonate and germanium dioxide were used in the ratios of 2 : 1 and 3 : 1. The raw material mixtures were thoroughly mixed and ground in an agate mortar until they passed completely through a sieve with 4900 openings/cm<sup>2</sup>.

The mixtures were moistened with 8-10% water, pressed into samples having the shape of prisms with dimensions of 1 × 1 × 3 cm<sup>3</sup> and sintered on platinum in a silite furnace: the mixture with a composition of 2CaO · GeO<sub>2</sub> at 1400° and the mixture with composition 3CaO · GeO<sub>2</sub> at 1500°.

Sintering of the mixture 2CaO · GeO<sub>2</sub> was done under conditions corresponding to those applied in the synthesis of the clinker mineral belite: the temperature was gradually raised to 1400° and kept at that level for three hours. After the temperature had been kept constant for this length of time, the sintered cake was rapidly cooled either by dipping it into water or by cooling it precipitately in air at 0°. The cooled sintered cake was ground and small prisms were formed from it. These prisms were subjected to renewed sintering. The procedure described was repeated until there was complete binding of the calcium oxide and formation of a homogeneous single-mineral product. The completeness of conversion in the germanates being synthesized was checked by determining the free calcium oxide. To accomplish this the well known ethyl glycerate method [5] was used. The total duration of sintering at 1400° amounted to six hours when sudden cooling with water was applied and to nine hours when rapid cooling with air was applied. The C<sub>2</sub>Ge which had been synthesized was dissolved in a 5% solution of boric acid according to the procedure described by E. I. Nagerova [6], just like dicalcium silicate.

The dicalcium germanate prepared in this manner was subjected to microscopic examination (Table 1), thermographic investigation (Fig. 1), and x-ray diffraction investigation (Fig. 2). Furthermore the binding properties of the substance were investigated.

The microscopic investigation indicated that there is similarity between the crystal-optical properties of the synthetic dicalcium germanate and those of  $\beta$ -dicalcium silicate. The x-ray diffraction diagrams as well as the thermograms showed that there is a fairly close correspondence between the interlayer distances of dicalcium germanate and those of  $\beta$ -dicalcium silicate.

The synthesized minerals 2CaO · GeO<sub>2</sub> and  $\beta$ -2CaO · SiO<sub>2</sub> were finely ground until they passed completely through a sieve with 4900 openings/cm<sup>2</sup>. They were then mixed with water until a plastic dough of normal consistency was obtained. The minerals then hardened and solidified.

TABLE 1. Crystal - Optical Characteristics of Dicalcium Germanate and of the  $\gamma$  and  $\beta$ -Modifications of Dicalcium Silicate

Mineral	Formula	Color	Index of refraction	Birefringence	Optical characteristic; optical sign	Crystallographic habit
Dicalcium germanate rapidly cooled with water, $t = 1400^\circ$	$2\text{CaO} \cdot \text{GeO}_2$ ( $\text{C}_2\text{Ge}$ )	Light with a greenish tinge	$n_q = 1.734$ $n_p = 1.700$	0.034	Biaxial, about $80^\circ +$	Rounded or rhombic grains
Dicalcium germanate rapidly cooled with air at $0^\circ$ , $t = 1400^\circ$	$2\text{CaO} \cdot \text{GeO}_2$ ( $\text{C}_2\text{Ge}$ )	Light-colored with a slight pink tinge	$n_q = 1.734$ $n_p = 1.700$	0.034	Biaxial, about $80^\circ +$	Rounded or rhombic grains
Dicalcium germanate prepared by V. F. Zhuravlev, $t = 1250^\circ$	$2\text{CaO} \cdot \text{GeO}_2$ ( $\text{C}_2\text{Ge}$ )	Light with a greenish tinge	$n_q = 1.734$ $n_p = 1.724$	0.010	-	Rounded grains or rectangular prisms
Dicalcium silicate, $\gamma$ -modification	$\gamma\text{-}2\text{CaO} \cdot \text{SiO}_2$ ( $\gamma\text{-C}_2\text{S}$ )	Light-colored	$N_q = 1.654$ $N_p = 1.642$	0.012	$60^\circ +$	Prisms
Dicalcium silicate, $\beta$ -modification	$\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$ ( $\beta\text{-C}_2\text{S}$ )	Light	$N_q = 1.735$ $N_p = 1.717$	0.018	Biaxial, large +	Rounded grains or rhombic prisms

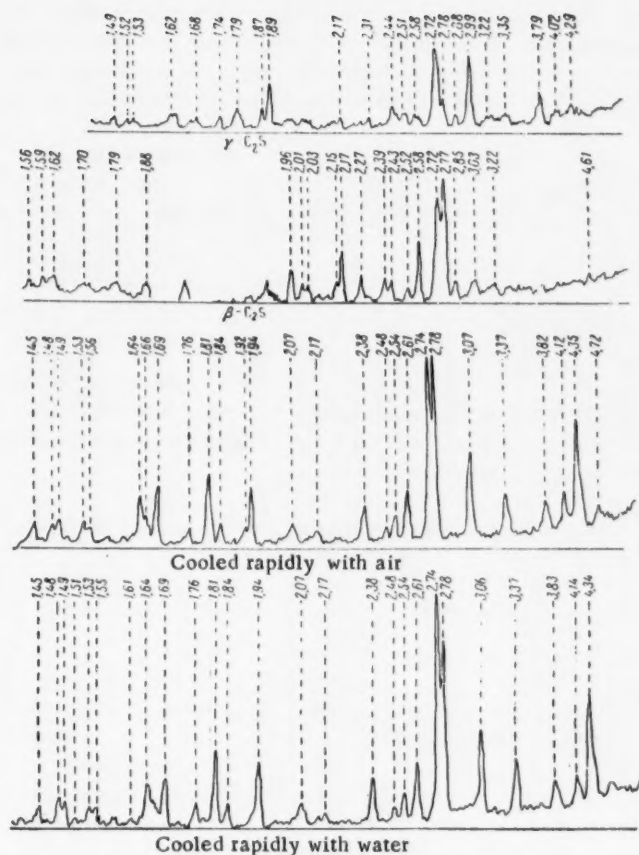
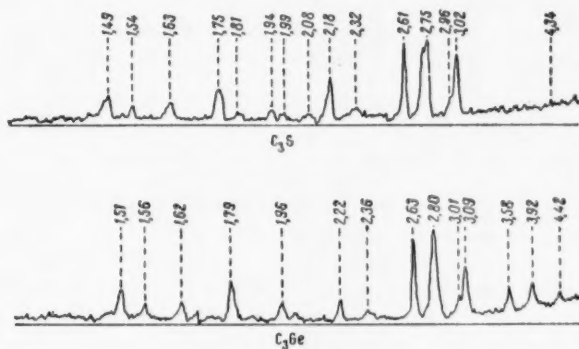
Fig. 2. X-ray diffraction diagrams of dicalcium germanate and of the  $\gamma$  and  $\beta$  modifications of dicalcium silicate.

Fig. 3. X-ray diffraction diagrams of tricalcium germanate and tricalcium silicate.

On sintering of the mixture  $3\text{CaO} \cdot \text{GeO}_2$  there was first formation of dicalcium germanate. The dicalcium germanate combined at high temperatures with free calcium oxide, forming tricalcium germanate. The sintering was carried out in a silite furnace by raising the temperature slowly to  $1500^\circ$  and keeping it then at this level for four hours. The sintered product was subjected to rapid cooling with air. The cooled sintered cake was ground, formed again into small prisms, and subjected to another sintering. Sintering was repeated 3-4 times until a homogeneous product was obtained. The phase composition of which was established by microscopic observation. The final product was checked for the absence of free calcium oxide.

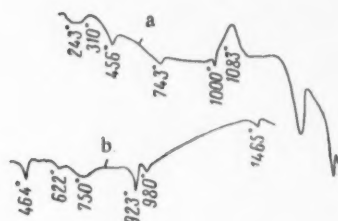


Fig. 4. Differential heating curves of tricalcium germanate (a) and tricalcium silicate (b).

As a result of sintering for 12-16 hours at  $1500^\circ$ , a homogeneous single-mineral product was obtained, the composition of which corresponded to  $3\text{CaO} \cdot \text{GeO}_2$ . This product consisted of a rather dense sintered cake which was light-colored and exhibited a yellow-green tinge.

The results of the microscopic investigation are compiled in Table 2, from which one can see that the crystal-optical properties of tricalcium germanate resembled those of tricalcium silicate.

TABLE 2. Crystal-Optical Properties of Tricalcium Germanate and Tricalcium Silicate

Mineral	Formula	Color	Refraction index	Birefringence	Optical characteristic; optical sign	Crystal structure	Crystallographic habit
Tricalcium germanate rapidly cooled with air at $0^\circ$	$3\text{CaO} \cdot \text{GeO}_2$ ( $\text{C}_3\text{Ge}$ )	Light-colored with a yellowish tinge	$n_q = 1.759$ $n_p = 1.754$	0.005	—		
Tricalcium silicate	$3\text{CaO} \cdot \text{SiO}_2$	Light-colored with a yellowish tinge	$N_q = 1.723$ $N_p = 1.717$	0.006	Low or zero minus	Hexagonal	Hexagonal prisms

The tricalcium germanate that had been prepared was sintered again and then cooled slowly. Microscopic examination established that under these conditions  $3\text{CaO} \cdot \text{GeO}_2$  decomposed partly into  $2\text{CaO} \cdot \text{GeO}_2$  and  $\text{CaO}$ . This was confirmed by the fact that the diffraction indices were  $n_q = 1.734$  and  $n_p = 1.700$ . The dicalcium germanate grains which formed had a hexagonal or oval shape.

X-ray diffraction investigation of the synthesized  $3\text{CaO} \cdot \text{GeO}_2$  with the application of an ionization apparatus (Fig. 3) confirmed that there was formation of the mineral  $3\text{CaO} \cdot \text{GeO}_2$ , which is closely related to  $3\text{CaO} \cdot \text{SiO}_2$ . It did not exhibit a line corresponding to  $\text{CaO} \cdot \text{SiO}_2$ .

On the high-temperature thermogram of tricalcium germanate (Fig. 4) one can see an endo-effect at  $456^\circ$  which is apparently associated with the loss of water of hydration at the surface  $\text{CaO}$  grains. The effect apparent on the curve at  $t = 743^\circ$  may be produced, just as in the case of tricalcium silicate [7] by a change of dicalcium germanate to another modification. This is confirmed by the presence of two intense endo-effects at  $1360^\circ$  and  $1454^\circ$ . The effect at  $1000^\circ$  is apparently characteristic for certain transformations of tricalcium germanate. The tricalcium germanate which had been prepared behaved just like tricalcium silicate in that it completely soluble in a 5% solution of boric acid.

The mineral  $3\text{CaO} \cdot \text{GeO}_2$  which had been synthesized was powdered finely until it passed completely through a sieve with 4900 openings/ $\text{cm}^2$ . The powder was mixed with water until a dough of normal consistency was obtained. There was rapid setting and hardening. The setting was completed within approximately 15 minutes.

The results obtained in the work give an experimental confirmation of the existence of tricalcium germanate, an analogon of tricalcium silicate. The crystal structure of tricalcium germanate was investigated. It was established that this substance has binding properties.

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# CONCERNING THE CONSTITUTIONAL DIAGRAM OF THE SYSTEM ALUMINUM-BORON

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The first systematic study of the system aluminum-boron was carried out in 1925 by Haenni [1], who subjected to thermographic investigation alloys of aluminum with boron containing up to 8.5% of boron by weight and discovered the formation of a eutectic at 565°. By extrapolation the composition of the eutectic was found to correspond to a boron content of approximately 15-18%. Fuss [2] and Meissner [3] extrapolated the liquidus curve to 50% of boron (Fig. 1). Hofmann and Jäniche [4] in 1936, by applying microscopic and x-ray diffraction methods, established the formation at 658° of a eutectic containing 0.2% of boron. They also established that there is strong rise of the melting point of aluminum when the content of boron has been increased to 4% and that there is a peritectic horizontal line at 1350°. The fact that the alloys in question melt at high temperatures prevented these authors from carrying on the investigation of the constitutional diagram. According to data in reference [1], the  $AlB_2$  phase disintegrates at 1100°, whereas according to reference [4] this phase forms as a result of a peritectic reaction taking place at 1350°.  $AlB_{12}$  was found to crystallize in several modifications [5, 6], the conditions of existence of which had not yet been subjected to investigation. Kohn, Katz, and Giardini [7] established the existence of still another phase, which had a composition corresponding to  $AlB_{10}$ .

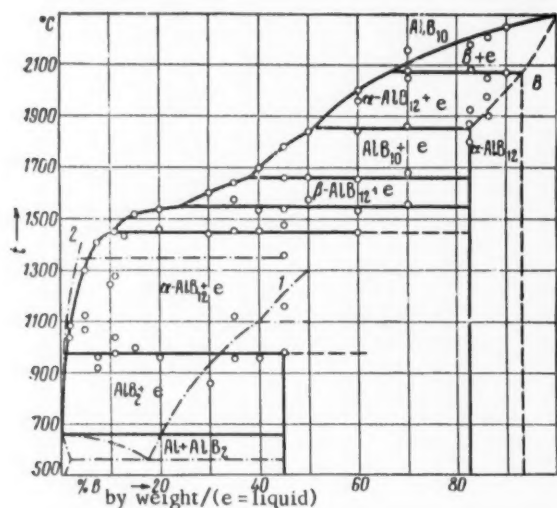


Fig. 1. Constitutional diagram of the system aluminum-boron. Dot-dash curves: 1) Haenni's data supplemented by Fuss and Meissner; 2) Hofmann and Jäniche's data. Solid curve corresponds to our data.

whereas according to reference [4] this phase forms as a result of a peritectic reaction taking place at 1350°.  $AlB_{12}$  was found to crystallize in several modifications [5, 6], the conditions of existence of which had not yet been subjected to investigation. Kohn, Katz, and Giardini [7] established the existence of still another phase, which had a composition corresponding to  $AlB_{10}$ .

The far from complete and contradictory data on the constitutional diagram of this system and also the practical importance of aluminum-boron phases from the standpoint of their application as semiconductors [8] and abrasives [9] make obvious the necessity of a further investigation of this system.

## Methods Applied in the Investigation

To investigate the constitutional diagram, we assembled a VNTA-1 installation of N. A. Nedumov's design [10] for high temperature contactless thermal analysis. Use of this equipment makes it possible to conduct thermal analyses at temperatures up to 2800°C. The samples in the form of pressed rods weighing 5 g each were prepared from aluminum having a purity of 99.99% and boron having a purity of 99.5% (0.16% of H, 0.26% of O).

After the samples had been placed in crucibles of corundum or BeO, they were brought to melting in an atmosphere consisting of purified helium and then cooled together with the furnace at a rate of 20° per minute. Both simple and differential recordings were made. In the case of alloys containing more than 50% of boron only the heating curves were recorded, because the crucibles reacted with the samples to some extent after the latter had been melted.



All phases isolated in a pure state were analyzed for their aluminum and boron content. Their density as established by pycnometric measurements was also determined. Some of the alloys were subjected to chemical analysis after the thermographic investigation. The analytical data showed that the difference between the intended composition and the actually obtained composition comprised  $\pm 0.3\%$ . The samples in their final state were subjected to x-ray phase analysis. The x-ray exposures were made by using filtered Co K $\alpha$  and Cu K $\alpha$  radiation and by employing cameras having a diameter of 86mm. Asymmetric placing of the film was applied.

### Results of the Investigation

A general view of the diagram is given in Fig. 1, from which one can see that the constitutional diagrams of the system aluminum-boron is that of a complex system which undergoes a number of peritectoid transformations. The initial course of the liquidus curve is the same as that reported by Hofmann and Jäniche. However, this curve is located somewhat lower. The lattice constant of aluminum calculated on the basis of the (420) reflection amounts to 4.041 kX, while this constant for aluminum-boron alloys amounts to 4.040 kX. Consequently, the changes in the lattice period of aluminum are within the limits of experimental error. For this reason no conclusions can be made in regard to the solubility of boron in aluminum on the basis of x-ray diffraction data. The authors of [4] arrived at the same conclusion. It was merely established that there is some broadening of the lines at large angles. In samples containing up to 1% of B, aluminum and AlB<sub>2</sub> were found to be present. At a higher content of boron,  $\alpha$ -AlB<sub>12</sub> was found to be present in addition of AlB<sub>2</sub>. The temperature of formation of the eutectic was determined and found to be in agreement with data given in [4].

The peritectic line at 975° corresponds to the decomposition AlB<sub>2</sub>  $\rightarrow$  AlB<sub>12</sub> + Al. However, at lower temperatures the alloys appeared to have a high degree of instability, because we detected  $\alpha$ -AlB<sub>12</sub> in them. The quantity of  $\alpha$ -AlB<sub>12</sub> increased with increasing contents of boron. The compound AlB<sub>2</sub> crystallized in the form of thin hexagonal plates having a bronze color. The dimensions of the lattice were  $a = 3.01 \text{ \AA}$ ,  $c = 3.26 \text{ \AA}$ . The density determined pycnometrically was 3.09 g/cm<sup>3</sup>.

In samples quenched from temperatures in the range of 1000-1400° we established the presence of Al and of  $\alpha$ -AlB<sub>12</sub>, the tetragonal modification of "graphite boron."

As can be seen in Fig. 1, the liquidus line rises steeply from the aluminum side. At a composition corresponding to 11% of B, it forms an inflection and gives rise to a peritectic horizontal line at 1450°. Evidently this is the same horizontal line which was located by Hofmann and Jäniche [4] at 1350°. This is confirmed by the fact that Lihl and Jenitschek [11] reported for this line a temperature higher than 1400°. Some samples with boron contents of 13, 15, 20, and 35% were quenched from 1500°. After the aluminum had been dissolved in hydrochloric acid, thin plates of a bronze color were obtained which resembled AlB<sub>2</sub> as far as their external appearance was concerned. An x-ray powder diffraction diagram which was taken coincided in almost every respect with a diffraction diagram of AlB<sub>2</sub>, except for the presence of some weak lines. Because of the presence of impurities we were not able to conduct a chemical analysis or to determine the density of the product. Thus, the nature of the transformations taking place at 1450° has not yet been clarified.

The peritectic at 1550° corresponded to the formation of  $\beta$ -AlB<sub>12</sub>, i.e. of "diamond-like boron." From samples having different boron contents up to 82.5% and quenched from 1600° we isolated this phase in a pure state. It crystallized in the form of tetragonal prisms or bipyramids. The color ranged from yellow to brown. The lattice constants coincided with those reported by Naray-Szabo [6]. The density determined pycnometrically was found to be 2.60 g/cm<sup>3</sup>. One must note that Naray-Szabo found carbon in the products investigated by him and reported the composition of the phase in question to be C<sub>2</sub>Al<sub>3</sub>B<sub>44</sub> or 3AlB<sub>12</sub>  $\cdot$  2B<sub>4</sub>C. We did not carry out an analysis for carbon. However, the syntheses were conducted under conditions which excluded contamination with carbon. Furthermore, the starting materials were of high purity and the chemical analysis of the pure phase indicated a boron content of 82.98% and an aluminum content of 16.85% (in some instances the composition was not stoichiometric; for instance, one of the samples was found to contain 86.0% of B and 14.1% of Al). Evidently the carbon found by Naray-Szabo was an impurity introduced by way of the initial material or during the aluminothermic reaction. The temperature region within which this phase exists is 1550-1660°, according to our diagram. On slow cooling this phase was transformed into  $\alpha$ -AlB<sub>12</sub>. When the sample was cooled slowly but not sharply enough the transformation  $\beta$ -AlB<sub>12</sub>  $\rightarrow$   $\alpha$ -AlB<sub>12</sub> did not proceed to completion. Examination under a binocular magnifying glass then showed the presence of needle-like yellow prisms with black edges, which indicated that the peritectic reaction was not completed.

In samples quenched from 1700-1750° we found the  $\text{AlB}_{10}$  reported by Kohn, Katz, and Giardini. This phase was obtained in the form of black pyramidal crystals. The density determined pycnometrically was  $2.72 \text{ g/cm}^3$ . The contents of boron and aluminum comprised 79.8 and 19.8%, respectively. The temperature range of existence of the phase was 1660-1850°. On slow cooling the  $\text{AlB}_{10}$  in the samples in question was transformed into  $\alpha\text{-AlB}_{12}$ . Quenching from temperatures in the range of 1850-2070° and slow cooling of an alloy having the composition of 82.5% of B and 17.5% of Al yielded  $\alpha\text{-AlB}_{12}$ . The lattice periods were  $\underline{a} = 10.15 \text{ \AA}$  and  $\underline{c} = 14.29 \text{ \AA}$ . The density determined pycnometrically was found to be equal to  $2.62 \text{ g/cm}^3$ . The  $\alpha\text{-AlB}_{12}$  phase was found to be present in alloys having a boron content of 82.5-93%. According to the constitutional diagram, this phase represents a solid solution of aluminum in boron. This is confirmed by the discovery of the existence of a tetragonal boron modification [12] which exhibits dimensions of the elementary cell that are very close to those of  $\alpha\text{-AlB}_{12}$ .

To check the data obtained by thermal analysis we prepared a number of samples by the method of arc melting in a helium atmosphere. The samples prepared in this manner had the following composition: 1) 70% of B, 30% of Al; 2) 75% of B, 25% of Al; 3) 80% of B, 20% of Al; 4) 82.5% of B, 17.5% of Al; 5) 86% of B, 14% of Al; 6) 91% of B, 10% of Al; 7) 96% of B, 4% of Al; and 8) amorphous boron with a purity of 99.5%.

The results of chemical analyses showed that the alloys deviated to some extent from the intended composition because of partial evaporation of aluminum and boron. The samples with a boron content up to approximately 82% consisted of aluminum and  $\alpha\text{-AlB}_{12}$ . In the concentration range from 82% to 93% of boron only  $\alpha\text{-AlB}_{12}$  was present in these samples. The boron that been melted in the arc furnace proved to be rhombohedral. The dimensions of the hexagonal cell determined on the basis of reflections at angles of  $78^\circ 7'$  and  $78^\circ 58'$  proved to be  $a = 10.95 \text{ \AA}$  and  $c = 23.76 \text{ \AA}$ , which was in agreement with data reported in reference [13].

In the concentration range of 93-100% of B we found only one phase, i.e. the rhombohedral boron referred to above. The dimensions of the elementary cell for a boron alloy containing 93% of boron were found to be  $\underline{a} = 10.95 \text{ \AA}$  and  $\underline{c} = 23.87 \text{ \AA}$ . Thus, the period  $\underline{c}$  increased by  $0.11 \text{ \AA}$ , which was apparently due to the formation of a solid solution of aluminum in boron.

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# THALLIUM POLYCHROMATES

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Chromates are among the least soluble compounds of thallium, and, therefore, they are of great value in the separation of thallium from solution both in commercial processes and in analytical chemistry. There has not been as yet any systematic investigation of thallium chromates. There have been only isolated, sometimes contradictory reports on the formation of thallium chromate, dichromate, and trichromate [1-6]. The composition, conditions of formation, and the physicochemical properties of all possible thallium isopolychromates are not reliably known. We investigated the heterogeneous equilibria in the system  $\text{Tl}_2\text{CrO}_4 - \text{CrO}_3 - \text{H}_2\text{O}$  at  $25^\circ$  with the aim of determining the

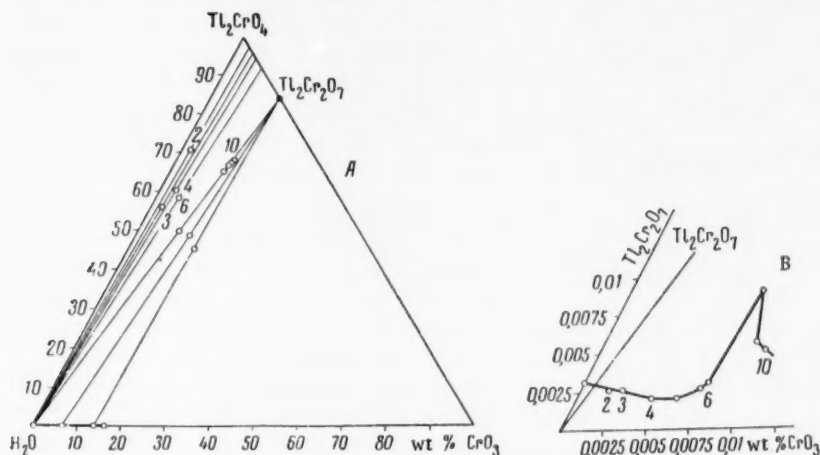


Fig. 1. A) Equilibrium diagram of the system  $\text{Tl}_2\text{CrO}_4 - \text{CrO}_3 - \text{H}_2\text{O}$  at  $25^\circ$ . B) Solubility isotherm in the region of very low concentrations.

compositions and solubilities of the thallium polychromates. The equilibrium diagram obtained for this system (Fig. 1) is characterized by the formation of incongruently soluble thallium dichromate and of solid solutions between thallium dichromate and chromate. Other polychromates of monovalent thallium are not formed in this system.

In order to verify literature reports of the existence of thallium trichromate [1-4] and also to verify the proposed formation of thallium polychromates in acid solutions [7], we separated the crystals from cooled solutions of thallium dichromate in sulfuric or nitric acid in accordance with the directions given in the literature [1-4]. The composition of the resulting crystals corresponded not to thallium trichromate, as previously considered, but to thallium dichromate (Fig. 3b):

Found %: Tl 65.40; 65.19; Cr 16.62; 16.64; Tl:Cr = 1.00:1.00; 1.00:1.00  $\text{Tl}_2\text{Cr}_2\text{O}_7$ .

Calculated %: Tl 65.43; Cr 16.65; Tl:Cr = 1:1.

No other thallium polychromates were separated from the acid solutions.

An investigation of heterogeneous equilibria in the systems  $\text{Tl}_2\text{Cr}_2\text{O}_7 - \text{Na}_2\text{Cr}_2\text{O}_7 - \text{H}_2\text{O}$ ,  $\text{Tl}_2\text{Cr}_2\text{O}_7 - \text{K}_2\text{Cr}_2\text{O}_7 - \text{H}_2\text{O}$ , and  $\text{Tl}_2\text{Cr}_2\text{O}_7 - (\text{NH}_4)_2\text{Cr}_2\text{O}_7 - \text{H}_2\text{O}$  at 25° showed that chemical compounds and solid solutions among the components are not formed.

The branch of the solubility isotherm corresponding to the crystallization of solid solutions based on thallium chromate in the system  $\text{Tl}_2\text{Cr}_2\text{O}_7 - \text{CrO}_3 - \text{H}_2\text{O}$  is characterized by very low concentrations of chromium trioxide (Fig. 1B). The second branch of this same isotherm, which corresponds to the crystallization of thallium dichromate, extends into the region of significant concentrations of chromium trioxide (Figs. 1A and 2A). Extension of the solubility isotherm in the systems formed by thallium dichromate and sodium, potassium, or ammonium dichromate is due to the solubility of the latter in water (Fig. 2B-G). The solubility of thallium dichromate in solutions of chromium trioxide, as well as in solutions of sodium, potassium, and ammonium (and, apparently, lithium, rubidium, and cesium) dichromates, decreased to the practically complete disappearance of thallium from solution. Only in liquid phases of comparatively high chromium trioxide concentration or of ammonium and alkali metal dichromates does the concentration of thallium dichromate begin to increase somewhat (Fig. 2).

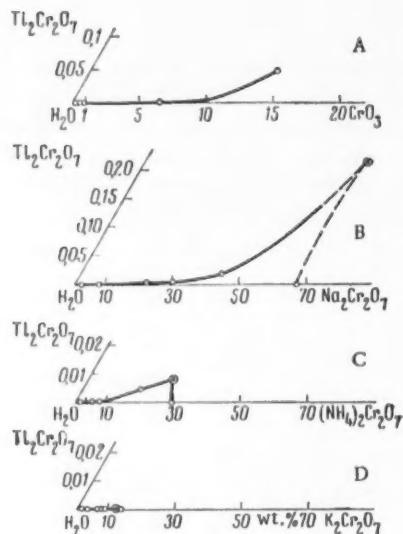


Fig. 2. Solubility isotherms in the systems: A)  $\text{Tl}_2\text{Cr}_2\text{O}_7 - \text{CrO}_3 - \text{H}_2\text{O}$ ; B)  $\text{Tl}_2\text{Cr}_2\text{O}_7 - \text{Na}_2\text{Cr}_2\text{O}_7 - \text{H}_2\text{O}$ ; C)  $\text{Tl}_2\text{Cr}_2\text{O}_7 - (\text{NH}_4)_2\text{Cr}_2\text{O}_7 - \text{H}_2\text{O}$ ; D)  $\text{Tl}_2\text{Cr}_2\text{O}_7 - \text{K}_2\text{Cr}_2\text{O}_7 - \text{H}_2\text{O}$ , all isotherms at 25°.

In solutions of chromium trioxide of relatively high concentration and also in concentrated solutions of sodium dichromate (the most soluble of the dichromates considered), the appearance in the liquid phase of monovalent thallium as a consequence of solution of thallium dichromate was accompanied by reciprocal oxidation-reduction reactions between monovalent thallium and hexavalent chromium. Therefore, liquid phases in the system  $\text{Tl}_2\text{Cr}_2\text{O}_7 - \text{Na}_2\text{Cr}_2\text{O}_7 - \text{H}_2\text{O}$  corresponding to crystallization of  $\text{Na}_2\text{Cr}_2\text{O}_7$  and also crystallization of  $\text{Tl}_2\text{Cr}_2\text{O}_7$  in regions of high concentration of sodium dichromate (Fig. 2B) contain an insignificant amount of trivalent thallium (and, consequently, an equivalent amount of trivalent chromium) along with monovalent thallium. In chromium trioxide solutions, the oxidation-reduction reaction between monovalent thallium and hexavalent chromium takes place at a greater rate, and at higher concentrations there is a change in the composition of both the liquid and solid phases. The interaction between thallium dichromate and chromium trioxide in this case naturally cannot be considered to fall within the limits of an investigation of the ternary system.

During the course of the heterogeneous interaction of thallium dichromate with chromium trioxide solutions having a concentration above about 30 wt. % (at 25°) there is a change in the solid phase; a new chemical compound, a previously unknown thallium polychromate, is formed. Thallium is present in this polychromate in two different valence states, one and three. The results of analyses of this thallium polychromate (when equilibrium had been reached between the liquid and solid phase) are in good agreement with the values calculated for  $\text{Tl}[\text{TlCr}_2\text{O}_8]$ :



Found %: Tl (I) 31.64; 31.42; Tl (III) 32.02; 31.44; Cr (VI) 16.22; 15.70

Tl (I): Tl (III): Cr (VI) = 1.00 : 1.01 : 2.01; 1.00 : 1.00 : 1.96 Tl [TlCr<sub>2</sub>O<sub>8</sub>].

Calculated %: Tl (I) 31.89; Tl (III) 31.89; Cr (VI) 16.23; Tl (I): Tl (III): Cr (VI) = 1:1:2

The formation of the complex anion [TlCr<sub>2</sub>O<sub>8</sub>]<sup>1-</sup> by incomplete oxidation of the thallium in thallium dichromate apparently takes place through the emergence of new bonds between trivalent thallium and oxygen.

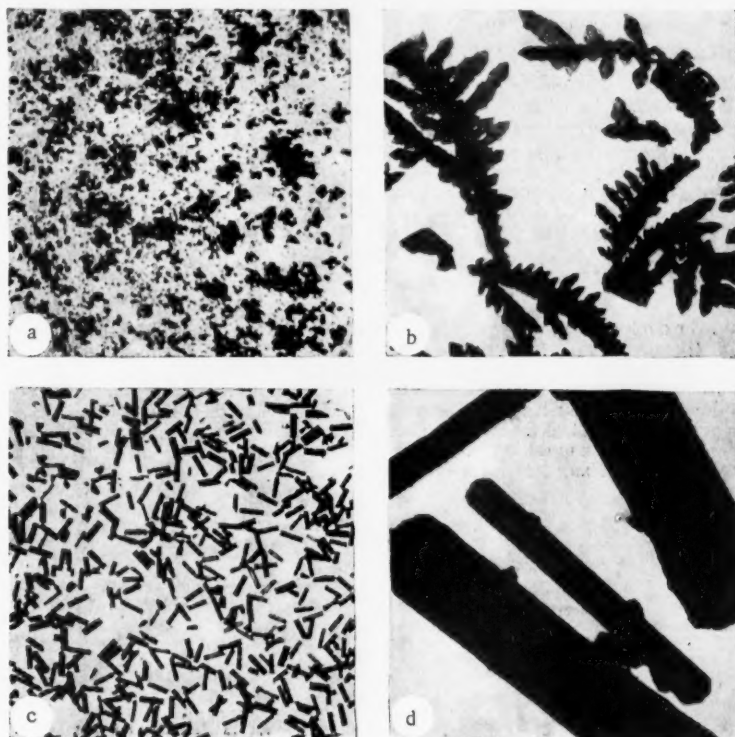


Fig. 3. Microphotographs of crystals (72 $\times$ ): a) Tl<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> precipitated by chromium trioxide; b) Tl<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> separated by cooling acid solutions supersaturated at the given temperature; c) and d) Tl [TlCr<sub>2</sub>O<sub>8</sub>].

The polychromate containing monovalent and trivalent thallium was separated as acicular crystals of different sizes with well-formed faces (Fig. 3 c and d). They are poorly soluble in water and are practically insoluble in organic solvents, particularly acetone and ethyl alcohol.

Consequently, isopolychromates of monovalent thallium are limited by the existence of thallium dichromate. However, the tendency of thallium toward the formation of complex compounds in which thallium is present in different valence states, which is a characteristic of thallium, is manifested in the thallium chromates, as is indicated by the formation of the polychromate containing monovalent and trivalent thallium.

The investigation of this previously unknown thallium polychromate continues.

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EVALUATION OF THE COMPARATIVE ELECTRONEGATIVITIES  
OF SUBSTITUENTS IN AROMATIC HETEROCYCLIC SYSTEMS  
BY A POTENTIOMETRIC METHOD

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(Presented by Academician A. N. Nesmeyanov, June 29, 1961)

Translated from *Doklady Akademii Nauk SSSR*, Vol. 141, No. 5,  
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The method of Lucas [1] is the most frequently used method of evaluating the effect of substituents on an aromatic nucleus. In this method, the strengths (pK) of benzoic acids substituted in the para position are measured, and the degree of electropositive or electronegative character of the substituents are estimated on the basis of the measurements. The method of Lucas, which is based on the views of Lewis [2], has been widely used, especially by Ingold and his school. However, it is not always easy to synthesize for a given substituent the corresponding para-substituted benzoic acid. Moreover, the strength of the acid depends not only on the interaction of the substituent with the benzene ring, but it is also determined to some extent by additional interaction of the ring with the carboxyl group, by intermolecular interaction, etc.

In investigating the properties of pyrazoles, we found that the basicity of the pyrazole ring depends directly on the nature of the substituent bonded to this ring.

Since the basicity of pyrazole is determined by the degree of basicity of the nitrogen atoms in the pyrazole ring, we have in this case the possibility of evaluating directly the density of the electron cloud formed by the six pi electrons of the aromatic ring (or in any case, that part of it in the vicinity of the nitrogen atoms). Pyrazoles are weak bases (approximating in basicity the dialkylanilines); therefore, in actual practice it has been found most convenient to measure the acidity of their sulfates rather than the basicity of the pyrazoles themselves. These sulfates partially hydrolyze, and the degree of hydrolysis and, correspondingly, the pH established in the solution characterize the basicity of the compound. By selecting such conditions, we practically excluded the effect of hydrogen bonds, which are readily formed by pyrazoles unsubstituted at the nitrogen, and we removed to a significant extent the effect of association of molecules and intermolecular interaction of functional groups, although of course we introduced the additional interaction of the sulfuric acid with the substituent. However, for the majority of substituents this interaction had practically no effect on the over-all picture of electron density distribution.

An LP-58 vacuum-tube potentiometer with glass and calomel electrodes was used in the work (standardization was carried out against a buffer solution with a pH of 7). An 0.005 mole sample of the substance being investigated was weighed with a precision of two units in the fourth place. The sample was dissolved in 25 ml of absolute methanol, 1 ml of 4.9732 N sulfuric acid was added from a microburette, and the pH was measured. It was shown by special experiments that an error in weighing of  $\pm 0.0005$  g and possible errors during measurements of the methanol and acid cause practically no change in the pH.\* The sulfuric acid itself had a pH of 0.42 under these conditions. The pH increased with the introduction of the sample, but not to a value above 3.5. The potentiometer used in this work usually has an accuracy of  $\pm 0.05$  pH units, but in comparative determinations and during the daily standardizations against the buffer solution the difference in the measurements did not exceed 0.02 pH units. The pH values cited below for solutions of 4-substituted dimethylpyrazoles and 5-substituted 1-phenyl-3-methylpyrazoles are averages of three determinations.

pH values for 4-substituted 3,5-dimethylpyrazoles were:  $\text{CH}_3$ , 3.47; H 3.12;  $\text{C}_6\text{H}_5\text{CH}_2$  3.02; I 1.27; Br 1.12; Cl 1.10;  $\text{CH}_3\text{CO}$  0.92; NO 0.58;  $\text{NO}_2$  0.47.

\* Laboratory technician T. A. Ivanova assisted in the work.

pH values for solutions of 4-substituted 1-phenyl-3,5-dimethylpyrazoles were: CH<sub>3</sub> 1.58; H 1.36; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> 1.28; Br 0.77.

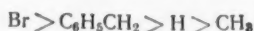
pH values for solutions of 4-substituted 1-heptyl-3,5-dimethylpyrazoles were: CH<sub>3</sub> 2.79; C<sub>2</sub>H<sub>5</sub> 2.73; C<sub>3</sub>H<sub>7</sub> 2.69; C<sub>4</sub>H<sub>9</sub> 2.68; H 2.35; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> 2.28; PyrCH<sub>2</sub>\* 1.78; CH<sub>3</sub>CONH 1.37; C<sub>6</sub>H<sub>5</sub>CONH 0.97; CHO 0.93; I 0.85; Br 0.74; Cl 0.71; CH<sub>3</sub>CO 0.66; C<sub>6</sub>H<sub>5</sub>CO 0.60; C<sub>2</sub>H<sub>5</sub>OCO 0.58; NO 0.57; NO<sub>2</sub> 0.57; NO<sub>2</sub> 0.50.

pH values for solutions of 5-substituted 1-phenyl-3-methylpyrazoles were: CH<sub>3</sub> 1.36; CH<sub>3</sub>S 1.25; C<sub>2</sub>H<sub>5</sub>O 1.22; H 0.63; α-furyl 0.61; Br 0.58; Cl 0.55; C<sub>6</sub>H<sub>5</sub>CO 0.54.

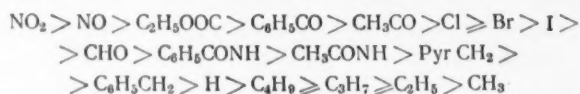
The results of the potentiometric measurements by the above method on the series of 4-substituted 3,5-dimethylpyrazoles showed that the substances can be arranged in a series in accordance with the degree of electronegativity of the substituents, and the series is in conformity with the series of Lucas:



When a phenyl group is substituted at a nitrogen of the nucleus, the over-all basicity of the compounds decreases, but the series is retained:



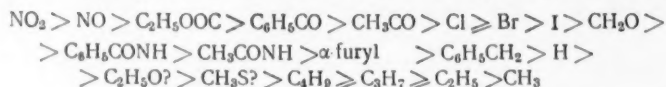
On the contrary, when an alkyl group is the substituent at the nitrogen (the rather large heptyl group was selected), the over-all basicity of the substances is correspondingly increased (in comparison to the N-phenyl substituted compounds) without disrupting the above series with respect to the effect of substituents in the 4-position:



When the substituent is present in another position, for example, the 5-substituted 1-phenyl-3-methylpyrazoles, the above relationship is still retained:



Thus, by summing up and comparing the above data, it is possible to establish the following series, in which all members of the series coming before hydrogen remove from the aromatic ring a portion of the electronic charge (as compared to the effect of hydrogen), and those coming after hydrogen increase the electronic charge of the ring:



The positions of the furyl radical and the C<sub>2</sub>H<sub>5</sub>O and CH<sub>3</sub>S groups in this series require additional work to establish them precisely. In connection with the weak basicity of the pyrazoles, when an electron-accepting substituent is present in the 4-position, the pyrazole system so weakly binds the protons that the pH of the mixture approaches that of the sulfuric acid alone in methanol. Thus, the scale of the measurements and, consequently, the differences in pH values are not the same at the beginning and the end of the series.

Thus, the difference between the basicities of solutions of 4-nitroso- and 4-nitropyrazoles is 0.04 pH unit, while a comparison of 4-methyl- and 4-butylpyrazoles reveals a difference in pH of 0.14; nevertheless, it cannot be concluded that the difference in basicity of the first pair of pyrazoles is less than that of the second pair.

Our proposed evaluation of the effect of various functional groups on the aromatic ring, which can be determined by measuring basicity or acidity by means of potentiometry, can evidently be extended to other heterocyclic systems also.

\* Bis (1-heptyl-3,5-dimethyl-4-pyrazolyl) methane.

The value of the method will be considerably greater with the use of potentiometers of a higher degree of accuracy. Moreover, our method, in which the effect of a substituent at the heterocyclic ring on the basicity (acidity) of the ring itself is measured, should detect finer differences due to changes in structure than do methods in which the effect of one substituent at the aromatic ring on another is evaluated. In our case, the length of the conjugated chain along which the effect is transmitted is shorter, and the mutual effect of substituent and ring should appear more clearly. For example, we actually found differences in the effects of iodine, bromine, and chlorine, which have not been observed when the evaluation was carried out by comparing two substituents.

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THE COMPARATIVE ACIDITY OF HYDROXYL GROUPS  
OF D-GLUCOSE,  $\alpha$ - AND  $\beta$ -METHYLGLUCOSIDES,  
MALTOSE, AND CELLOBIOSE

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(Presented by Academician M. M. Shemyakin, May 4, 1961)

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Data on the comparative acidity of carbohydrate hydroxyls are of particular interest in connection with the study of the reactivity of the individual hydroxyl groups of carbohydrate molecules, but practically no such data exists at the present time. Dissociation constants of the order of  $10^{-14}$ – $10^{-13}$  have been determined for certain carbohydrates by measuring the electrical conductivity of dilute alkaline solutions [1]. Attempts to determine the dissociation constants of hydroxyls of polysaccharides [2] have not given satisfactory results.

We have begun a study of the degree of dissociation of the hydroxyl groups of glucose and certain of its derivatives, specifically partially methylated glucoses, methylglucosides, and disaccharides. The present communication presents data obtained for D-glucose, methylglucosides, cellobiose, and maltose.

Acidity of the hydroxyls was determined by a nonaqueous titration method [3]. The electrometric titration was carried out at 20° in a medium of ethylenediamine with an 0.1 N solution of KOH. Metal oxide electrodes [4] were used.\* The measuring circuit consisted of molybdenum indicator electrode and a calomel reference electrode. The galvanometer was an M-198 type with a sensitivity of  $10^{-8}$  amp, while the electrolyte bridge was a saturated solution of KCl. The circuit included a resistance of the order of 1 meg. Solutions with concentrations of 0.1, 0.01, and 0.001 N and 0.001 M of the appropriate substance in ethylenediamine were used in the investigation. The molybdenum indicator electrode, the saturated KCl bridge, a glass stirrer, and the end of a burette containing the titrant were immersed in the solution. The system was completely isolated from air during the titration. The comparative dissociation of the hydroxyls of the substance was determined from the value of the current at the equivalence points. The clearest curves were obtained from titrations of 0.001 N solutions of the carbohydrates, when it was possible to back-titrate the least dissociating hydroxyls. All of the substances investigated behaved as polybasic acids in the ethylenediamine medium, as was indicated by the presence of several inflection points on the titration curves. In order more clearly to determine the equivalence points obtained during titration of the carbohydrates, which are, in effect, mixtures of acids or of individual polyfunctional compounds, curves showing the relationship between the derivative of the current with respect to volume of the titrant and the volume of the titrant were plotted. The resulting curves for the titration of 0.001 N solutions of the carbohydrates are shown in Fig. 1. Several peaks are apparent on all curves. These peaks characterize the equivalence points of the different hydroxyls. In glucose, for example, all five hydroxyls were titrated (Fig. 1). The titration curves show that acidity of the hydroxyls changes from glucose to glucoside, and it depends both on the nature of the aglucon (the methyl group or the second monosaccharide molecule in disaccharides) and on the type of bond ( $\alpha$  or  $\beta$ ).

There are at present no data which will permit one to relate all equivalence points to specific hydroxyls of the carbohydrate molecule. However, there is a basis for the assumption that the anomeric hydroxyl and the hydroxyl at C<sub>2</sub> are the most acidic. The acidic properties of the anomeric hydroxyl appear clearly in the reaction by which glycosides are formed, which takes place similarly to the interaction of alcohols with the hydroxyl of a carboxyl group. The increased acidity of the hydroxyl at the second carbon atom (C<sub>2</sub>) is apparently due to the proximity of

\* The authors' thanks are due O. M. Podurovskaya for consultation and assistance in establishing the method used.



the acetal group, and it appears in the increased reactivity of this hydroxyl in glycosides and polysaccharides in reactions with bases [5].

The first and highest peaks on the titration curves of glucose, maltose, and cellobiose, which characterize the degree of dissociation of the anomeric hydroxyls, differ greatly from each other. In order to obtain a stricter comparison of the degree of dissociation of the anomeric hydroxyls of glucose, maltose, and cellobiose, titration of 0.001M solutions of these compounds, in which the concentrations of anomeric hydroxyls are the same, were carried out. These compounds can be arranged in the following series of decreasing degree of dissociation of the anomeric hydroxyl: D-glucose > cellobiose > maltose.

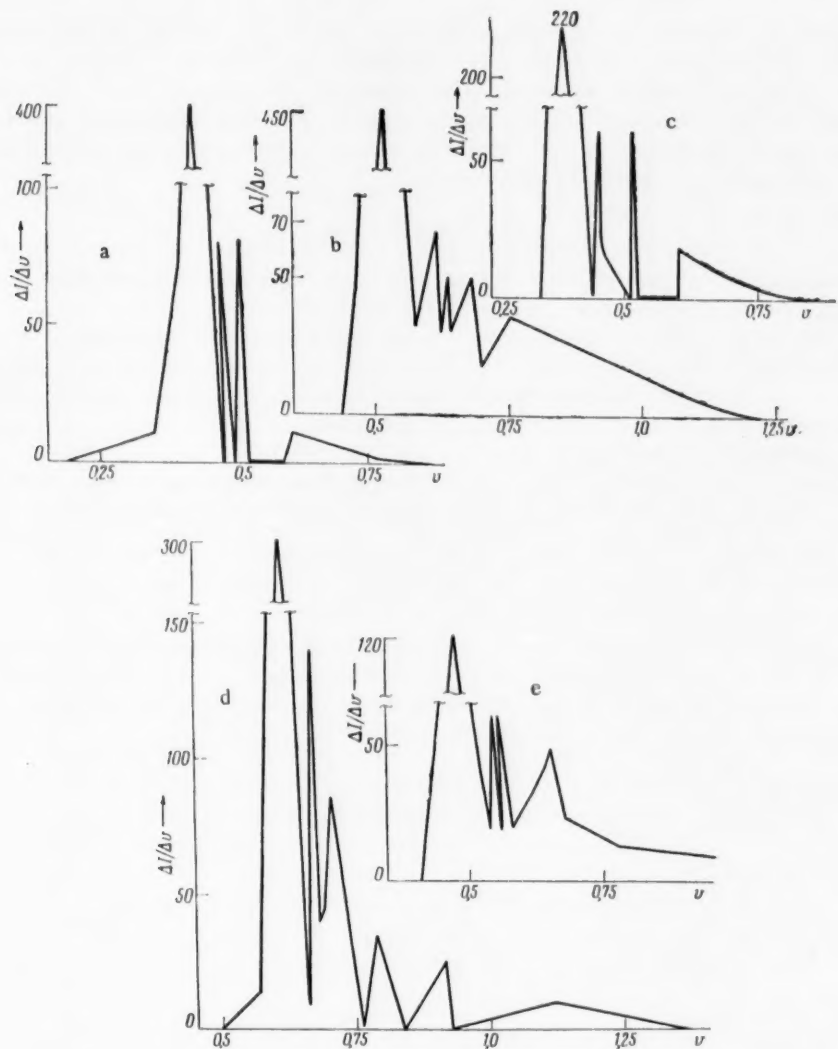


Fig. 1. Titration curves for 0.001 N solutions of  $\beta$ -methylglucoside (a), D-glucose (b),  $\alpha$ -methylglucoside (c), cellobiose (d), and maltose (e).

The first maxima on the titration curves of 0.001 N solutions of  $\alpha$ - and  $\beta$ -methylglucosides (Fig. 1) and the second maximum on the titration curves of glucose may be assigned to the hydroxyls at C<sub>2</sub>. The compounds may be arranged in the following series with respect to the degree of dissociation of the hydroxyl at C<sub>2</sub>:  $\beta$ -methyl-D-glucoside > cellobiose >  $\alpha$ -methyl-D-glucoside > maltose > glucose.

It follows from these data that with the transition from free glucose to the glucoside, the degree of dissociation of the hydroxyl at C<sub>2</sub> sharply increases, and the degree of dissociation of  $\beta$ -glucosides is significantly higher than the degree of dissociation of  $\alpha$ -glucosides. The nature of the aglucon also greatly affects the acidity of the hydroxyl at C<sub>2</sub>. Thus, the degree of dissociation of the hydroxyl at C<sub>2</sub> in  $\beta$ -methylglucoside is significantly higher than the degree of dissociation of the corresponding hydroxyl in cellobiose.

These results are in good agreement with the data which we obtained by comparing the reactivity of the hydroxyls of cellobiose ( $\beta$ -glucoside bonds) and of amylose ( $\alpha$ -glucoside bonds). As a consequence of the significantly higher acidity of the C<sub>2</sub> hydroxyls of cellobiose than of those of amylose, the reaction with bases proceeds almost selectively in the first stage – the reaction with the C<sub>2</sub> hydroxyl; such selectivity is not observed with amylose.

The reason for the variation in acidity of C<sub>2</sub> hydroxyls as a function of substitution at the glucoside center and of the configuration of the glucoside has not yet been established. However, it can be assumed that it is determined to a significant extent by the presence and strength of hydrogen bonds which arise between a substituent at C<sub>1</sub> and C<sub>2</sub>. Thus, for example, the higher degree of dissociation of the C<sub>2</sub> hydroxyl in  $\alpha$ -glucosides as compared to that for the  $\beta$ -isomer can be explained by the greater probability of the formation of a hydrogen bond between the C<sub>2</sub> hydroxyl and the oxygen of the glucoside group in the axial position.

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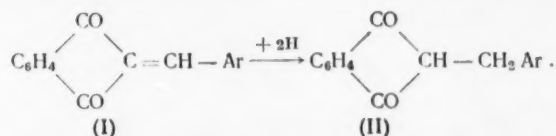
# SYNTHESIS OF 2-ARALKYL-1,3-INDANEDIONES BY CATALYTIC HYDROGENATION OF 2-ARALKYLIDEN-1,3-INDANEDIONES

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Original article submitted July 31, 1961

Many of the 2-substituted 1,3-indanediones are physiologically active substances. Thus, for example, 2-phenyl-1,3-indanedione is an active blood anticoagulant and is used in the Soviet Union under the name "phenylene" [1-3]. This same physiological effect is also possessed by other derivatives of 1,3-indanedione [4], of which the most active are 2- $\alpha$ -naphthyl-1,3-indanedione [5], 2-anisyl-1,3-indanedione ("anizidone") [6], and 2-hydroxymethyl-2-phenyl-1,3-indanedione ("omephine") [7]. Other 2-substituted 1,3-indanediones in which the aromatic radical is somewhat removed from the number 2 carbon atom, i.e., compounds of Type II, are also of interest in this connection. The simplest example of this type is 2-benzyl-1,3-indanedione (IIa), which is prepared by condensation of diethyl phthalate with an ester of hydrocinnamic acid [8]. Of the derivatives of 2-benzyl-1,3-indanedione, the literature describes only 2-(*p*-nitrobenzyl)-1,3-indanedione, which is prepared by cyclization of *p*-nitrobenzylbenzoylacetate [9, 10]. A series of investigations has established that it is impossible to prepare 1,3-indanedione [11], 2-benzylindanedione [9, 10], and 2-*p*-methoxybenzyl-1,3-indanedione by a similar cyclization.

We recently developed a new general method for the preparation of 2-aralkyl-1,3-indanediones (II) by selective hydrogenation of 2-aralkyliden-1,3-indanediones (I) with sodium dithionite (hydrosulfite,  $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) [12]:


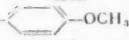

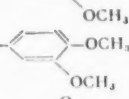
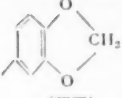


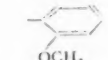


The initial 2-aralkyliden-1,3-indanediones (I) are easily prepared by condensation of aromatic aldehydes with 1,3-indanedione [13] or with the sodium salt of ethyl indanedione carboxylate [14]. This method has been successfully used to prepare various 2-methoxybenzyl-1,3-indanediones [15], aminobenzyl-1,3-indanediones [16], and also analogs of 2-aralkyl-1,3-indanediones in which the aryl radical is replaced by a five-member heterocyclic system (IIf and g) [17]. These compounds included substances possessing anticoagulant properties [4]. Unfortunately, the yields of aralkyl-1,3-indanediones obtained by sodium dithionite hydrogenation are not large. In order to improve the yields and to develop a preparative method for 2-aralkyl-1,3-indanediones, we turned to a study of catalytic hydrogenation of 2-aralkyliden-1,3-indanediones. It was, of course, necessary to find an appropriate catalyst which would selectively hydrogenate the carbon-carbon double bond in an  $\alpha, \beta$ -position to the carbonyl group without reduction of the latter. Our attention was drawn to a communication by Japanese authors who were able to carry out selective hydrogenation of the carbon-carbon double bond of benzalacetone, mesityl oxide, and a number of other  $\alpha, \beta$ -unsaturated ketones by hydrogenation in the presence of a skeletal nickel catalyst with the addition of potassium iodide or other metal halides [18-22]. The literature [23] has reported that an analogous selectivity during hydrogenation of  $\alpha, \beta$ -unsaturated ketones can also be obtained by partial poisoning of the nickel catalyst with methyl iodide. We used a similar method for the catalytic hydrogenation of aralkylidenindanediones. Hydrogenation was systematically studied under different conditions using benzal-1,3-indanedione (Ia) as the hydrogenatable compound. It was found that hydrogenation of 0.015 mole of I in alcoholic solution in the presence of skeletal nickel (W-2 grade) with the addition of potassium iodide at a temperature of 60-65° and ordinary pressure results in 2-benzyl-1,3-indanedione (IIa) with a yield of 70.6% (hydrogenation with sodium dithionite [12] resulted in a yield of only 19.1%). Other 2-aralkyl-1,3-indanediones (IIb to e) and also their analogs with heterocyclic radicals (IIf and g) were prepared simi-

larly (and also usually with better yields). The reaction conditions and yields are shown in Table 1. The products obtained by catalytic hydrogenation were identical with the 2-aralkyl-1,3-indanediones (and their heterocyclic analogs) prepared by hydrogenation with sodium dithionite [12, 15, 17].

The structure of 2-benzyl-1,3-indanedione (IIa) and 2-*p*-methoxybenzyl-1,3-indanedione (IIb) were also confirmed by infrared absorption spectroscopy (in the solid state). It is known [24] that the diketo form of 1,3-indane-

TABLE 1

Ar	Ni <sub>sk</sub> , g	KI, g	Vol. of alco- hol, ml	Reaction time, hrs.	Lit. source	Yield of II, % hydrogen- ation with Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	cat. hy- drogena- tion
a 	1	2,5	100	7,0	(12)	19,1	70,6
b 	1	2,5	100	5,5	(15)	31,0	52,6
c 	1	2,5	50	7,0	(15)	38,9	11,8
d 	3	5,0	100	6,5	(15)	15,0	38,4
e 	1	2,5	100	7,0	(15)	21,0	54,4
f 	1	2,5	100	12,0	(17)	26,0	54,4
g 	1	2,5	100	10,0	(17)	39,8	95,6
h 	1	—	50	6	(15)	45,9	89,0

Note: Reaction temperatures: a to g, 60-65°; z, 78°.

dione derivatives is characterized by a split band in the interval of 1705-1770  $\text{cm}^{-1}$  and by a frequency at 1580-1600  $\text{cm}^{-1}$ . The split band is assigned to the two carbonyl groups, while the second band is due to the aromatic system.

The i.r. spectrum of solid 2-benzyl-1,3-indanedione has two carbonyl bands, 1710  $\text{cm}^{-1}$  (94,3) and 1743  $\text{cm}^{-1}$  (76,8), as well as bands at 1592  $\text{cm}^{-1}$  (49,3) and 1602  $\text{cm}^{-1}$  (48) belonging to the aromatic ring. The i.r. spectrum of solid 2-*p*-methoxybenzyl-1,3-indanedione also has two carbonyl bands, 1706  $\text{cm}^{-1}$  (79) and 1736  $\text{cm}^{-1}$  (63), and the corresponding bands belonging to the aromatic ring, 1512  $\text{cm}^{-1}$  (63,5), 1588  $\text{cm}^{-1}$  (41,5), and 1614  $\text{cm}^{-1}$  (47).

In the case of 2-benzyl-1,3-indanedione (IIa) it is clear that the maximum yield is obtained when 0.015 mole of the original aralkylidenindanedione in 100 ml of alcohol is hydrogenated in the presence of 1 g of skeletal nickel and 2,5 g of potassium iodide.

A decrease in the potassium iodide leads to tar formation. When the hydrogenation is carried out without potassium iodide, the carbonyl groups are also reduced, and, depending on the reaction conditions, 2-benzyl-1-indanone-3-ol or 2-benzyl-1,3-indanediol can be obtained (a separate communication will be published on this). A similar phenomenon is also observed during hydrogenation of other 2-yliden-1,3-indanediones. The only exception was the hydrogenation of 2-*o*-methoxybenzal-1,3-indanedione (Ih). Hydrogenation of this compound under conditions analogous to the preceding resulted in only an insignificant absorption of hydrogen, and the yield of the corresponding 2-*o*-methoxybenzyl-1,3-indanedione (IIh) was very small. It was found that in this case the corresponding aralkylindanedione (IIh) can be obtained in good yield only under more vigorous reaction conditions, hydrogenation at the boiling point; moreover, a more active catalyst - skeletal nickel without added potassium iodide - is necessary in this case. It is evident that here a steric effect of the methoxy group in the ortho position has come into play, because *p*-methoxybenzal-1,3-indanedione (Ib) hydrogenated very readily.

Skeletal nickel catalyst with added potassium iodide does not hydrogenate 2-p-diethylaminobenzal-1,3-indanedione under analogous conditions, though it is hydrogenated by sodium dithionite with very good yield [16]; 2-o-hydroxybenzal-1,3-indanedione and 2- $\alpha$ -pyrrolal-1,3-indanedione are not hydrogenated either (nor is the latter hydrogenated by sodium dithionite [17]).

The experimental section of this paper gives a detailed description of the hydrogenation of 2-benzal-1,3-indanedione and 2-o-methoxybenzal-1,3-indanedione by way of example.

#### EXPERIMENTAL

**2-Benzyl-1,3-indanedione (IIa).** To a pear-shaped hydrogenation flask (300 ml volume) were charged 3.51 g (0.015 mole) of 2-benzal-1,3-indanedione, 100 ml of alcohol, 2.5 g of potassium iodide, and approximately 1 g of skeletal nickel catalyst (W-2 grade) [25] suspended in absolute alcohol. The flask was connected by rubber tubing to the lower end of a reflux condenser, the upper end of which was connected to a gas holder containing hydrogen. The air was purged from the system by a stream of hydrogen, leaving the flask via a second tube. This tube was then closed with a stopper through which a thermometer passed. The contents of the reaction vessel were agitated by means of a rocker and were heated by an infrared lamp. About 300 ml of hydrogen was absorbed during agitation at 60-65° for 7 hours. On the following day, the flask was disconnected, and the catalyst and unreacted starting material were removed by filtration. The filtrate was diluted with 400 ml of water, 10 ml of concentrated hydrochloric acid was added, and, after 3 hours, the resulting precipitate was separated by filtration. The yield was 2.5 g (70.6%). The 2-benzyl-1,3-indanedione melted at 94-96°, and crystallization from dilute (1 : 1) methanol did not change the melting point. A mixture with a known sample showed no depression of the melting point.

IIb-e were prepared similarly; hydrochloric acid was not used during separation of II-f-g from the reaction mixture.

**2-o-Methoxybenzyl-1,3-indanedione (IIh).** Hydrogenation of 3.96 g (0.015 mole) of 2-o-methoxybenzal-1,3-indanedione in 100 ml of alcohol in the presence of 1 g of skeletal nickel without the addition of potassium iodide was carried out in the apparatus described above at the boiling point of the solvent (78°) for 6 hours. The product, 3.55 g (89% yield) of 2-o-methoxybenzyl-1,3-indanedione, was separated in a manner similar to the above; after crystallization from a methanol - water mixture (2 : 1), it melted at 86-88°. A mixture with known 2-o-methoxybenzyl-1,3-indanedione [15] melted without depression of the melting point.

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# TITANIUM AND TIN TETRACHLORIDES AS RADICAL SCAVENGERS DURING RADIOLYSIS OF HYDROCARBONS

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(Presented by Academician S. S. Medvedev, July 14, 1961)

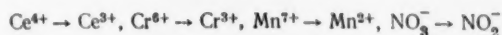
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pp. 1097-1100, December, 1961

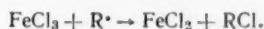
Original article submitted July 14, 1961

Dissolved substances which react with the primary radicals in ordinary stoichiometric ratios can be used to measure the yield of free radicals formed in radiation-induced chemical processes taking place in the liquid phase.

Thus, during radiolysis of aqueous solutions, the action of H atoms is usually associated with reduction of ions, for example [1-4]:



Ferrous iron in the presence of air [5, 6] or degassed aqueous solutions of divalent tin or trivalent titanium [7, 8] have been used as scavengers for oxidizing radiolysis components. Oxygen, iodine, diphenylpicrylhydrazyl, and vinyl compounds are usually used as radical scavengers during radiolysis of hydrocarbons. New possibilities for this purpose are compounds of metals of variable valence. When salts of metals of variable valence are used to scavenge radicals formed during radiolysis in organic media, the metal is reduced. Collinson and Cherniak showed this for the case of ferric chloride dissolved in methanol, acetone, or tetrahydrofuran [9, 10]. The iron was reduced according to the reaction:



The present work constituted a study of the radiation-induced reduction of titanium tetrachloride and of stannic chloride in hydrocarbon solutions under the influence of  $\gamma$ -radiation from a  $\text{Co}^{60}$  source and the possibility of using these reactions for initiating polymerization. Mixtures of  $\text{TiCl}_4$  and *n*-octane,  $\text{TiCl}_4$  and benzene,  $\text{SnCl}_4$  and *n*-octane, and  $\text{SnCl}_4$  and octamethylcyclotetrasiloxane were subjected to irradiation in sealed glass ampoules. The octamethylcyclotetrasiloxane was dried over  $\text{CaCl}_2$ . The  $\text{TiCl}_4$  was distilled over copper powder. The solutions were degassed by the usual melting - freezing operations under vacuum, after which the ampoules were evacuated and resealed. After removal of the liquid radiolysis products, the precipitates were dried under vacuum at  $120^\circ$ . The precipitates were then analyzed for lower chlorides by potentiometric titration with silver chloride and platinum electrodes.

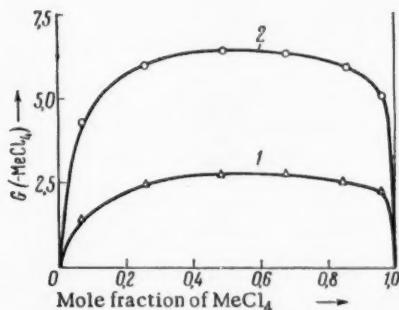


Fig. 1. Radiation yields in the reduction of  $\text{SnCl}_4$  (1) and  $\text{TiCl}_4$  (2) in *n*-octane solutions.

The amount of energy absorbed was determined by ferrousulfate dosimetry. The yield of the reaction was 15.6 molecules per 100 ev. The construction of an apparatus for radiation-induced reactions has been described previously [11]. The apparatus includes a  $\text{Co}^{60}$  source having an activity of 1440 g-eq of Ra. When the  $\text{TiCl}_4$  - hydrocarbon mixtures were irradiated, a brown flocculent, gradually thickening precipitate was formed. The radiation yield with respect to decrease in  $\text{TiCl}_4$ ,  $G(-\text{TiCl}_4)$ , for *n*-octane solutions are shown in Fig. 1, 2 as a function of  $\text{TiCl}_4$  concentration.  $G(-\text{TiCl}_4)$  was an order of magnitude lower in the case of the benzene solutions, and the maximum value reached was 0.75, in good agreement with the data of other authors [9] on the radiation yield of radicals formed during irradiation of benzene.

According to elemental analysis, the composition of the precipitates corresponded to  $TiCl_3$ . The precipitates were completely soluble in  $N,N$ -dimethylformamide.

The brown modification of  $\beta$ - $TiCl_3$  was formed, and this was used as one component of a Ziegler-type catalyst along with  $(iso-C_4H_9)_2AlCl$ . This catalyst exhibited normal activity for the polymerization of diolefins.

An electron paramagnetic resonance (EPR) spectrum obtained with  $TiCl_4$  -  $n$ -octane mixtures irradiated at 77°K evidently belongs to trivalent titanium. The  $Ti^{3+}$  ion is stable at the temperature indicated, and its spectrum, which was obtained along with the spectrum of the hydrocarbon, is shown in Fig. 2. The width of the line is 22 oe, measured between points of maximum slope. The  $g$  factor for the center of the signal was 1.91. The sensitivity was  $\sim 5 \cdot 10^{-12}$  M of diphenylpicrylhydrazyl. It is important to note that the intensity of the spectrum increased linearly with an increase in the concentration of  $TiCl_4$ . At the same time, the presence of an EPR spectrum due to H atoms stabilized on the quartz surface [12] was confirmed.

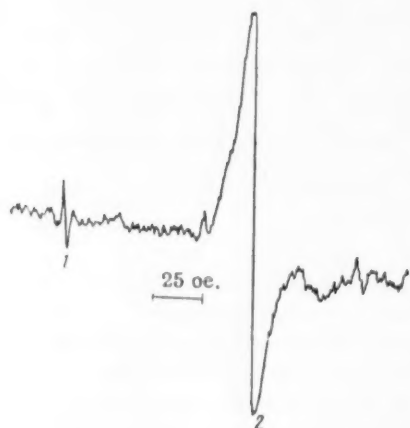


Fig. 2. EPR spectrum of solutions of  $TiCl_4$  in  $n$ -octane irradiated at 77°K: doublet due to H atoms (1) and  $Ti^{3+}$  spectrum (2). Dose: 3.5 million r.

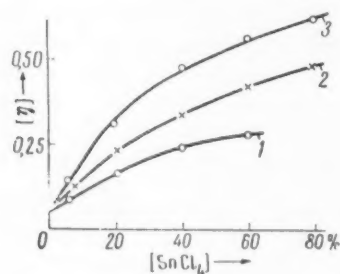


Fig. 3. Intrinsic viscosities of benzene solutions of polymer formed in the  $SnCl_4$  - octamethylcyclotetrasiloxane system. Radiation dose: 1)  $6.4 \cdot 10^6$ ; 2)  $2 \cdot 10^7$ ; 3)  $2.9 \cdot 10^7$  r.

The polymer was separated after filtration of the precipitated stannous chloride under an atmosphere of dry nitrogen and elimination of the unreacted stannic chloride. The molecular weight of the polymer increased with an increase in  $SnCl_4$  concentration (Fig. 3). The methane-to-hydrogen ratio in the gases evolved during irradiation of octamethylcyclotetrasiloxane alone remained constant over a wide dosage range up to 45 million r. Within this same dosage range, the addition of stannic chloride led to an increase in this ratio (Fig. 4).

Irradiation of  $SnCl_4$  - hydrocarbon mixtures led to precipitation of stannous chloride. The radiation yield with respect to decrease in  $SnCl_4$  ( $G(-SnCl_4)$ ) for the system  $n$ -octane -  $SnCl_4$  is shown in Fig. 1, 1 as a function of the composition of the mixture. The system stannic chloride - octamethylcyclotetrasiloxane is of particular interest. As Andrianov has shown [13], at temperatures of 120-150° stannic chloride is a catalyst for the polymerization of octamethylcyclotetrasiloxane accompanied by opening of the ring.

In this connection, it appeared possible to carry out this reaction at room temperature under the influence of ionizing radiation, and it also seemed that the polymerization would be accompanied by chlorination of the resulting polymer through reduction of the stannic chloride. We established that radiation of a mixture of octamethylcyclotetrasiloxane and stannic chloride at room temperature actually leads to polymerization of the octamethylcyclotetrasiloxane.

Moreover, the reduction  $Sn^{4+} \rightarrow Sn^{2+}$  took place accompanied by chlorination of the polymer. The chlorine content of the polymer reached 3 mole % at doses of about 30 million r.

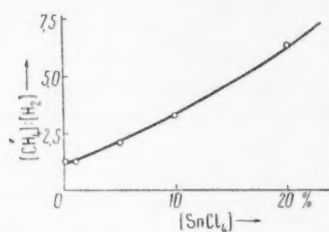
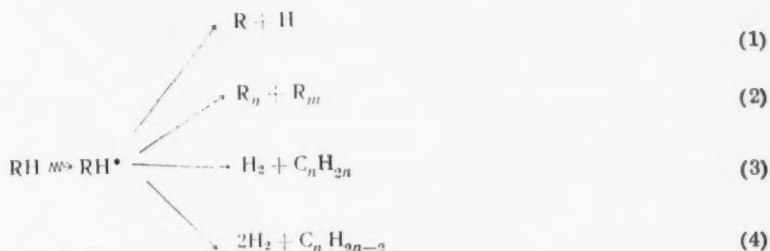


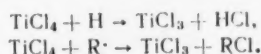
Fig. 4. Gas evolution during irradiation of  $SnCl_4$  - octamethylcyclotetrasiloxane mixtures. Radiation dose, 29.6 million r.

This indicates that the activity of a hydrogen atom is higher than that of a methyl radical in the reduction of stannic chloride under the influence of radiation.

On the basis of the above experimental data and of well-known concepts of the character of radiation-induced chemical reactions taking place in hydrocarbons [14], the following possible types of initial reactions can be contemplated:



The free radicals formed by reactions 1 and 2 can interact with  $\text{TiCl}_4$  and  $\text{SnCl}_4$ :



Moreover, one cannot exclude the possibility of redistribution the absorbed energy in this two-component system with an increase in the concentration of the titanium or tin tetrachloride.

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# DIELS - ALDER REACTIONS OF DIVINYL SULFOXIDE AND OF DIVINYL SULFONE WITH SYMMETRICAL DIENES

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(Presented by Academician B. A. Arbuzov, July 15, 1961)

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It is known that vinylalkyl and vinylaryl sulfones and thiovinyl ethers contain an active double bond and are capable of entering into Diels-Alder condensation with a number of dienes [1-4]. As a rule, unsaturated sulfoxides are less active than unsaturated sulfones in nucleophilic addition reactions, but they are more active than sulfides [5]. However, the ability of unsaturated sulfoxides to undergo Diels-Alder reactions has not as yet been studied.

It seemed to us to be of interest to consider the Diels-Alder reaction of divinylsulfoxide (I), which is of particular interest in that it contains two equivalent vinyl groups, so that changes in the ratio of reactants would be expected to result in the formation of both single and double addition products. With this aim, we have studied the Diels-Alder reaction of (I) with butadiene (II), 2,3-dimethyl-1,3-butadiene (III), and cyclopentadiene (IV). The reactions were carried out at different temperatures (100-185°) and with different ratios of diene to dienophile (see Table 1).

It was found that the ease with which (I) undergoes Diels-Alder addition with these dienes depends on the position of the diene in the usual activity series  $II < III < IV$ . However, divinyl sulfoxide reacts with cyclopentadiene to form both single and double addition products, depending on the ratio of reactants and the temperature, while with butadiene and 2,3-dimethyl-1,3-butadiene we were able to obtain only products of the addition at one vinyl group of the sulfoxide (see Table 2). An increase in reaction temperature, an increase in reaction time, and the use of a solvent containing an excess of the diene did not yield a double addition product. In connection with this, it seemed to be of undoubted interest to study the reactivity of divinyl sulfone (V) in similar reactions. It was found that, in contrast to I, divinyl sulfone gives two series of adducts, not only with IV, but also with II and III (see Table 2). Thus, the absence of dienophilic activity of the vinyl group in the single adducts of divinyl sulfoxide still remains obscure and requires further study. I and V and their single and double adducts

TABLE 1

Expt. no.	Dienophile : diene ratio, mole	Reaction temp., °C	Reaction, hr.	Yield, %
1	I : II = 0,078 : 0,29	140-145	20	27
2	I : III = 0,078 : 0,158	135-140	8	36
3	I : IV = 0,051 : 0,045	95-100	1,5	90
4	I : IV = 0,078 : 0,157	140-145	7	72
5	V : II = 0,051 : 0,047	100-110	8	78
6	V : III = 0,034 : 0,024	70-75	3	72
7	V : IV = 0,051 : 0,045	70-75	2	45
8	V : II = 0,038 : 0,184	130-135	9	100
9	V : III = 0,034 : 0,072	130-132	5	98
10	V : IV = 0,019 : 0,045	170-185	9	60



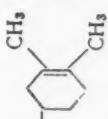

were characterized and the presence of a free vinyl group in the single adducts was established by means of infrared spectroscopy (see Table 3).

E. N. Prilezhaeva and co-workers [6] have reported the frequencies of C = C bond valence vibrations for a series of vinyl alkyl sulfoxides, and they noted that these frequencies are appreciably lower than the frequencies of the C = C bond valence vibrations of olefinic hydrocarbons. As Table 3 shows, these frequencies are still lower in the case of divinyl sulfoxide and divinyl sulfone and their single addition products:  $\nu_{C=C}$  1607  $\text{cm}^{-1}$  in the sulfone and 1595  $\text{cm}^{-1}$  in the sulfoxide. The presence of an absorption band in the region of C = C valence vibrations and of a band assignable to out-of-plane deformation vibrations of the C - H bond of the methylene group in  $\text{RCH}=\text{CH}_2$  (960 - 930  $\text{cm}^{-1}$ ) in the spectra of the single adducts indicates the retention of one free vinyl group.

In addition, the appearance of a rather intense absorption band in the region of 1651  $\text{cm}^{-1}$ , which is characteristic of C = C valence vibrations in the cyclohexene ring, and in the region of 1569  $\text{cm}^{-1}$  which is characteristic of



TABLE 2

Expt. no.	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R	Name of adduct	B.p., °C at 1.5- 2.10 <sup>-2</sup> mm	M.p., °C	<sup>20</sup> n <sub>D</sub>	<sup>20</sup> d <sub>4</sub>	MRD		C, %		H, %		S, %		Empirical formula
	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.			
Diels-Alder addition products of divinyl sulfone																			
1	H	H	H	H	—CH=CH <sub>2</sub>	3-Cyclohexenyl vinyl sulfone	75--78	—1	1.5449	1.1176	44, 20	44, 84	61, 22	61, 53	7, 70	7, 69	19, 83	20, 51	C <sub>8</sub> H <sub>12</sub> O <sub>2</sub> S
2	H	H	CH <sub>3</sub>	CH <sub>3</sub>	—CH=CH <sub>2</sub>	3,4-Dimethyl- 3-cyclohexenyl vinyl sulfone	76--80	—	1.5358	1.0586	54, 22	53, 95	65, 91	65, 16	8, 90	8, 75	16, 57	17, 39	C <sub>10</sub> H <sub>16</sub> O <sub>2</sub> S
3	H	CH—H	H	H	—CH=CH <sub>2</sub>	Bicyclo [2,2,1]- 3-heptenyl vinyl sulfone	85--87	—	1.5454	1.1246	47, 34	47, 13	—	—	—	—	19, 10	19, 05	C <sub>8</sub> H <sub>12</sub> O <sub>2</sub> S
4	H	CH—H	H	H		Bis(bicyclo [2, 2,1]-3-heptenyl) sulfone	122--126	84	—	—	—	—	72, 08	71, 73	7, 68	7, 69	12, 96	13, 68	C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> S
Diels-Alder addition products of divinyl sulfone																			
1	H	H	H	H	—CH—CH <sub>2</sub>	3-Cyclohexenyl vinyl sulfone	86--90	—	1.5120	1.1646	44, 37	44, 61	—	—	—	—	18, 28	18, 61	C <sub>8</sub> H <sub>12</sub> O <sub>2</sub> S
2	H	H	H	H		Bis-3-cyclo- hexenyl sulfone	141	—	—	—	—	—	63, 45	63, 68	8, 13	8, 02	13, 65	14, 81	C <sub>12</sub> H <sub>18</sub> O <sub>2</sub> S
3	H	H	CH <sub>3</sub>	CH <sub>3</sub>	—CH=CH <sub>2</sub>	3,4-Dimethyl- 3-cyclohexenyl vinyl sulfone	100--103	—	1.5119	1.1325	53, 13	53, 85	—	—	—	—	15, 85	16, 01	C <sub>10</sub> H <sub>16</sub> O <sub>2</sub> S
4	H	H	CH <sub>3</sub>	CH <sub>3</sub>		Bis(3,4-di- methyl-3- cyclohexenyl) sulfone	152.5- 153	—	—	—	—	—	—	—	—	—	11, 12	11, 35	C <sub>16</sub> H <sub>26</sub> O <sub>2</sub> S
5	H	—CH <sub>2</sub> —H	H	H	—CH—CH <sub>2</sub>	Bicyclo [2,2,1]- 3-heptenyl vinyl sulfone	110--112	—	1.5247	1.2136	46, 50	47, 03	—	—	—	—	17, 24	17, 40	C <sub>8</sub> H <sub>12</sub> O <sub>2</sub> S
6	H	—CH <sub>2</sub> —H	H	H		Bis(bicyclo [2, 2,1]-3-hep- tenyl) sulfone	76	—	—	—	—	—	67, 49	67, 12	7, 31	7, 25	12, 26	12, 81	C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> S

\* Group refractions used: 8.70 for SO and 8.60 for SO<sub>2</sub> (calculated from the data of the present work).

\*\* Analysis for sulfur was carried out by the method of N. V. Sokolova and V. A. Orestova [19] as improved by NIRP.

the bicycloheptene ring, indicates the formation of these rings [7]. Absorption bands characteristic of a free vinyl group were not present in the spectra of the double adducts.

The authors express their appreciation to E. G. Yarkova and R. M. Mamina for recording the infrared spectra.

# EXPERIMENTAL

The divinyl sulfoxide was prepared by the method described by Ford-Moore [5]. B. p., 61°/4 mm;  $n_D^{20}$  1.5143;  $d_4^{20}$  1.0800. Literature data: b. p., 67-68°/5-6 mm;  $n_D^{20}$  1.5100;  $d_4^{20}$  1.0810.

TABLE 3. Spectral Characteristics of Single Adducts of Divinyl Sulfoxide and Divinyl Sulfone

Expt. No.	Name of adduct	$\nu_{cm^{-1}}$	Frequency assignment
1	3-Cyclohexenyl vinyl sulfoxide	1651 s	Valence vibrations of C = C bond of cyclohexene ring
		1593 av	Valence vibrations of C = C of vinyl group
		1036 v. s.	Valence vibrations of S-O bond
		960, 932 v. s.	Out-of-plane deformation vibrations of C-H of vinyl group
2	Bicyclo [2,2,1]-3-heptenyl vinyl sulfoxide	1598 av	Valence vibrations of C = C of vinyl group
		1569 w.	Valence vibrations of C = C of bicycloheptene ring
		1048 v.s.	Valence vibrations of S-O bond
		960, 930 s	Out-of-plane deformation vibrations of C-H of vinyl group
3	3-Cyclohexenyl vinyl sulfone	1647 av	Valence vibrations of C = C of cyclohexene ring
		1607 av	Valence vibrations of C = C of vinyl group
		1300 v.s.	Asymmetric SO <sub>2</sub> vibrations
		1124 v.s.	Symmetric SO <sub>2</sub> vibrations
		979, 935 s	Out-of-plane deformation vibrations of C-H of vinyl group
4	3,4-Dimethyl-3-cyclohexenyl vinyl sulfone	1648 w.	Valence vibrations of C = C of cyclohexene ring
		1610 a. v.	Valence vibrations of C = C of vinyl group
		1307 v. s.	Asymmetric SO <sub>2</sub> vibrations
		1120 v. s.	Symmetrical SO <sub>2</sub> vibrations
		974, 930 s	Out-of-plane deformation vibrations of C-H of vinyl group
5	Bicyclo [2,2,1]-3-heptenyl vinyl sulfone	1613 a.v.	Valence vibrations of C = C of vinyl group
		1569 w.	Valence vibrations of C = C of bicycloheptene ring
		1305 v.s.	Asymmetric SO <sub>2</sub> vibrations
		1115 v.s.	Symmetric SO <sub>2</sub> vibrations
		974, 951 s	Out-of-plane deformation vibrations of C-H of vinyl group

Note: v s) very strong; a v) average; w) weak.

The divinyl sulfone was synthesized by the method of Overberger and co-workers [8]. B. p., 104-105°/10 mm;  $n_D^{20}$  1.4772;  $d_4^{20}$  1.1781. Literature data for divinyl sulfone [9]: b.p., 110°/17 mm;  $n_D^{20}$  1.4782;  $d_4^{20}$  1.1790.

The Diels-Alder reactions were carried out in an atmosphere of CO<sub>2</sub> in the presence of hydroquinone in sealed tubes. The reaction conditions are given in Table 1. All single adducts of both divinyl sulfoxide and divinyl sulfone were thick, oily liquids, while the double adducts were white acicular crystals. The double adducts were recrystallized from a 1 : 2 mixture of benzene and petroleum ether. All of the double adducts were readily soluble in acetone, benzene, and carbon disulfide, moderately soluble in chloroform and carbon tetrachloride, difficultly soluble in ether, and insoluble in petroleum ether and gasoline-range hydrocarbons.

The infrared spectra were recorded with IKS-14 (3000 cm<sup>-1</sup> region, LiF prism) and H-800 Hilger (700-2000 cm<sup>-1</sup> region, NaCl prism) double-beam spectrometers with a film or CCl<sub>4</sub> solution.

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THE ADDITION OF DIALKYL PHOSPHITES TO  
3,3'-DIMETHOXY-4,4'-BIPHENYL DIISOCYANATE  
DIPHENYLMETHANE 4,4'-DIISOCYANATE

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S. M. Kirov Kazan Chemical Technological Institute

(Presented by Academician B. A. Arbuzov, June 26, 1961)

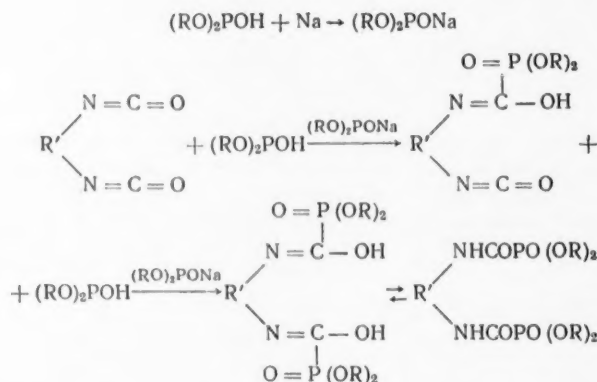
Translated from Doklady Akademii Nauk SSSR, Vol. 141, No. 5,

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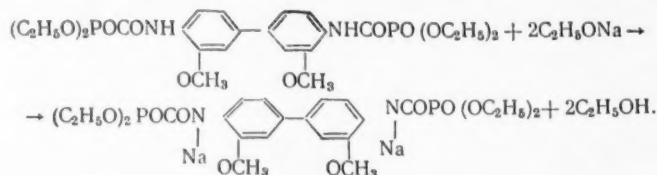
We have previously shown that dialkyl phosphites readily add to 1,5-naphthylene, 1,6-hexamethylene, and 2,4-tolylene diisocyanates in the presence of sodium alcoholate [1-2]. In a continuation of our investigations along this line, we decided to study the addition of dialkylphosphites to 3,3'-dimethoxy-4,4'-biphenyl diisocyanate and diphenylmethane 4,4'-diisocyanate.

It was found that dialkyl phosphites readily add to these diisocyanates in the presence of a very small amount of sodium. The interaction of diisocyanates with dialkyl phosphites may be represented in general form by the following equations:



The mechanism of this reaction is analogous to that of the interaction of dialkyl phosphites with 1,5-naphthylene diisocyanate in the presence of sodium alcoholates.

The equilibrium is greatly shifted in the direction of the keto form [3]. Thus, for example, the action of sodium ethylate on a benzene solution of the diethyl ester of 3,3'-dimethoxy-4,4'-biphenylamidophosphonoformic acid [3,3'-dimethoxybiphenyl-4,4'-bis(carbamoylphosphonic) acid] yields the sodium derivative in accordance with:





In this case, sodium ethylate reacts with the keto form of the addition product. Our investigation along this line continues. With the exception of products Nos. 9-12 (Table 1), all of these substances crystallized on prolonged standing.

The products were purified by two low-temperature recrystallizations from methyl alcohol. These white crystalline substances were readily soluble in alcohol, benzene, dioxane, acetone, etc. They were insoluble in water. The properties of the addition products are shown in Table 1.

TABLE 1



Expt. no.	R	M.p., °C*	Phosphorous content, %		Nitrogen content, %		Yield, %	Empirical formula
			found	calc.	found	calc.		

$(RO)_3 POCONH$    $-CH_2-$    $NHCOPO(OR)_3$

1	CH <sub>3</sub>	155—156	12,92	13,19	5,74	5,95	70	C <sub>19</sub> H <sub>24</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub>
			12,80		5,70			
2	C <sub>2</sub> H <sub>5</sub>	115—116	11,40	11,78	5,21	5,32	76	C <sub>23</sub> H <sub>32</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub>
			11,45		5,18			
3	n-C <sub>3</sub> H <sub>7</sub>	88—89	10,53	10,65	4,67	4,81	83	C <sub>27</sub> H <sub>40</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub>
			10,50		4,57			
4	iso-C <sub>3</sub> H <sub>7</sub>	178—179	10,62	10,65	4,70	4,81	88	C <sub>27</sub> H <sub>40</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub>
		with very slight decomp.	10,45		4,68			
5	n-C <sub>4</sub> H <sub>9</sub>	68—70	9,49	9,71	4,19	4,38	66	C <sub>31</sub> H <sub>48</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub>
			9,38		4,23			
6	iso-C <sub>4</sub> H <sub>9</sub>	102—103	9,51	9,71	4,09	4,38	84	C <sub>31</sub> H <sub>48</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub>
			9,37		4,13			
7	ClCH <sub>2</sub> CH <sub>2</sub>	111—113	9,04	9,33	3,96	4,21	85	C <sub>23</sub> H <sub>28</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub> Cl <sub>4</sub>
			9,00		4,08			

$(RO)_2 POCONH$    $-$    $NHCOPO(OR)_2$

8	CH <sub>3</sub>	102—104	11,77	12,01	5,12	5,42	62	C <sub>20</sub> H <sub>26</sub> O <sub>10</sub> N <sub>2</sub> P <sub>2</sub>
			11,86		5,09			
9	C <sub>2</sub> H <sub>5</sub>	148—150	10,38	10,83	4,45	4,89	68	C <sub>24</sub> H <sub>34</sub> O <sub>10</sub> N <sub>2</sub> P <sub>2</sub>
			10,49		4,67			
10	iso-C <sub>3</sub> H <sub>7</sub>	146	9,76	9,86	4,45	4,45	79	C <sub>28</sub> H <sub>42</sub> O <sub>10</sub> N <sub>2</sub> P <sub>2</sub>
			9,70		4,27			
11	iso-C <sub>4</sub> H <sub>9</sub>	125—126	8,92	9,06	3,93	4,09	84	C <sub>32</sub> H <sub>50</sub> O <sub>10</sub> N <sub>2</sub> P <sub>2</sub>
			8,64		3,86			
12	ClCH <sub>2</sub> CH <sub>2</sub>	127—128	8,37	8,73	3,61	3,94	86	C <sub>24</sub> H <sub>30</sub> O <sub>10</sub> N <sub>2</sub> P <sub>2</sub> Cl <sub>4</sub>
			8,33		3,48			

\* The melting points were determined in sealed capillaries.

We have thus studied the addition of dialkyl phosphites to 3,3'-dimethoxy-4,4'-biphenyl diisocyanate and diphenylmethane 4,4'-diisocyanate. In conclusion, the authors acknowledge their indebtedness to B. M. Tsigina for the gift of the diisocyanates used in this investigation.

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# THE REACTION OF KETENE WITH MERCURY SALTS

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(Presented by Academician A. N. Nesmeyanov, June 9, 1961)

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In a continuation of our investigation of methods for the synthesis of  $\alpha$ -mercuricarboxylic acids and of their reactivity, we have studied the possibility of preparing compounds of this type from ketene. Considering the high activity of ketene, it would be expected that mercury alcoholates [1] would readily react with it with the formation of esters of mercurated acetic acid. As a matter of fact, when ketene was passed into a suspension of mercury alcoholate in ether, the reaction proceeded readily and with the evolution of heat, an organomercury compound was formed. In contrast to known addition reactions in which mercury salts add at double and triple carbon-carbon bonds (alkenes, dienes, enol esters) and in which the resulting organomercury salts are of the type  $RHgX$ , in this case the reaction proceeds to the formation of the total organomercury compound  $R_2Hg$  owing to the high reactivity of ketene:



It was established that the reaction is more conveniently carried out by starting not with mercury alcoholates, which have been described only for the simplest alcohols [1], but with solutions or suspensions of mercuric acetate in the appropriate alcohol:



In carrying out the reaction, an excess of ketene should be passed into the reaction mixture in order to convert the initially formed compound,  $CH_3COOHgCH_2COOR$ , to  $Hg(CH_2COOR)_2$ , since a mixture of these compounds cannot be successfully resolved by crystallization in a number of cases. Finally, compounds of the type  $Hg(CH_2COOR)_2$  can also be prepared by reacting ketene with mercuric oxide with the addition of a small amount of mercuric acetate to the reaction mixture. Initially, the mercuric acetate reacts with the ketene as described above. Acetic acid is formed along with the organomercury compound, and this dissolves the mercuric oxide, replacing the mercury salt which has reacted with ketene. This variant of the reaction is the most convenient one, since in this case the total organomercury compound is formed contaminated by only traces of the organomercury salt  $CH_3COOHgCH_2COOR$ . The reaction of ketene with mercuric oxide in the presence of mercuric acetate was studied in various alcohols - methyl, ethyl, normal propyl, isopropyl, butyl alcohols, etc. In all cases, compounds of the type  $Hg(CH_2COOR)_2$  were obtained in yields close to quantitative.

Esters of mercuribisacetic acid are crystalline compounds; they are readily soluble in the usual organic solvents. The majority of the esters of mercuribisacetic acid can be recrystallized from ether. The methyl ester of mercuribisacetic acid is readily soluble in water and can be recovered from aqueous solution unchanged. The following compounds of the type  $Hg(CH_2COOR)_2$  were prepared (R, the melting point, the Hg content in per cent, both found and calculated, are listed):  $CH_3$ , 100°, 57.99%, 58.05%, 57.85%;  $C_2H_5$ , 40°, 53.98%, 53.21%, 53.52%;  $n-C_3H_7$ , 46°, 49.86%, 49.61%, 49.80%;  $iso-C_3H_7$ , 33°, 50.27%, 50.36%, 49.80%;  $n-C_4H_9$ , 38-39°, 46.95%, 46.98%, 46.55%;  $iso-C_4H_9$ , 72°, 47.15%, 46.97%, 46.55%;  $tert-C_4H_9$ , 86°, 46.80%, 46.95%, 46.55%.

Esters of mercuribisacetic acid readily react with mercuric chloride in a reverse symmetrization reaction yielding compounds of the type  $ClHgCH_2COOR$  (R, the melting point, the Hg content in percent, both found and calculated, are given; compounds marked with an asterisk were prepared previously by another method [2]):  $CH_3$ , 83°, 65.02%, 65.06%, 64.88%;  $C_2H_5^*$ , 66°, -,  $C_3H_7^*$ , 57°, -,  $iso-C_3H_7$ , 59°, 59.29%, 59.28%, 59.49%;  $n-C_4H_9$ , 20-22°, 57.04%, 57.09%, 57.11%;  $iso-C_4H_9$ , 65°, 57.30%, 57.50%, 57.11%.

## EXPERIMENTAL

The reaction of mercury methylate with ketene. A filtered solution of 16 g of mercuric acetate in 160 ml of absolute methanol was added dropwise (with stirring) to a solution of sodium methylate (from 2.3 g of sodium and 40 ml of absolute methanol). The precipitated mercury methylate was separated by centrifugation and washed with absolute methanol and ether; absolute ether was added, and, with vigorous stirring, passage of ketene into the reaction mixture was begun. The reaction proceeded exothermically. The light yellow, solid mercury methylate disappeared, and crystals of the methyl ester of mercuribisacetic acid began to separate from the dark solution. The crystals were dissolved by adding ether, and the solution was filtered. Evaporation of the ether yielded 13 g (75% of theoretical) of the methyl ester of mercuribisacetic acid. After recrystallization from a mixture of methanol and ether, the compound melted at 100°.

Found %: C 20.52; 20.63; H 2.82; 2.71; Hg 57.99; 58.05;  $C_6H_{10}O_4Hg$ .

Calculated %: C 20.78; H 2.91; Hg 57.85.

The reaction of mercuric acetate with ketene. A 3-4-fold excess of ketene was passed into a solution of 32 g of mercuric acetate in 120 ml of absolute methanol. After filtration and evaporation of the solution under water aspirator vacuum there remained crystals and some oil (total weight 33 g, i.e. 95% of theoretical). The material was purified by two recrystallization from methanol, and 18 g (52% of theoretical) of the methyl ester of mercuribisacetic acid with an m. p. of 98° was obtained; after a third recrystallization from a mixture of methanol and ether, the compound melted at 100°. A mixture with known methyl ester of mercuribisacetic acid melted without depression of the melting point.

The reaction of mercuric oxide with ketene in the presence of mercuric acetate. Ketene was passed, with stirring, into a suspension of 20 g of mercuric oxide and 3 g of mercuric acetate in 120 ml of absolute methanol until the mercuric oxide was completely dissolved. After filtration, the solution was evaporated cold, and 34 g of the methyl ester of mercuribisacetic acid (96.5% of theoretical) with an m. p. of 96-98° was obtained. After recrystallization from methanol, the compound melted at 100°, and a mixture with known methyl ester of mercuribisacetic acid showed no depression of the melting point.

The reaction of the methyl ester of mercuribisacetic acid with mercuric chloride. A solution of 3.9 g of the methyl ester of mercuribisacetic acid and 3 g of mercuric chloride in 13 ml of methanol was heated at 70° to the complete disappearance of  $HgCl_2$  (test with NaOH). The solution was filtered and cooled, and 6 g of the methyl ester of chloromercuriacetic acid (89% of theoretical) with an m. p. of 82-83° precipitated; after recrystallization from methanol, the compound melted at 83°.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# THE EFFECT OF COMPLEX FORMATION ON THE SEPARATION OF ELEMENTS BY COCRYSTALLIZATION

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Chromatography, extraction, and cocrystallization are the methods most frequently used at present for the separation of chemically similar elements. The use of complex formation has significantly increased the effectiveness of the first two methods. Moreover, there has been a series of publications [1-3] reporting that separation of elements by cocrystallization can be improved by the use of complexons. However, the published material is purely empirical, and no attempts have been made to use it as a basis for theoretical calculations of the effectiveness of separation. The single exception is the work reported in reference [4], on the basis of which a calculation of the cocrystallization coefficient in the presence of a complex former can be made. However, the authors considered a case rarely encountered in actual practice - the case in which the microelement forms a complex compound with the given ligand. The case in which both components taking part in the cocrystallization form complex compounds is of enormously greater interest.

It is well known that the distribution of the microelement between the crystalline phase and the solution obeys Khlopkin's law [5]:

$$\frac{x}{y} = D_0 \frac{[A^*]}{[A'^*]}, \quad (1)$$

where  $x$  and  $y$  are the amounts of microelement and macroelement in the precipitate;  $[A^*]$  and  $[A'^*]$  are the contents of the components in the solution;  $D_0$  is the cocrystallization coefficient. This coefficient lies in the interval  $0 < D_0 < \infty$ . The more  $D_0$  differs from 1, the better is the separation of the elements.

With the introduction of a complex former into the solution, complex compounds of the microelement and macroelement having different stabilities are formed, which leads to a change in the ratio  $[A^*]/[A'^*]$ , and this, in turn, has an effect on the experimentally determined coefficient  $D$ .

In order for the precipitate to be in equilibrium with the solution, it is only necessary for a part of the macroelement to be bound in the complex. In considering those systems in which only one of the complex compounds formed by the macroelement and the microelement has high stability, it will be recognized that this compound will predominate over a wide range of ligand concentration. In this case, the amount of macroelement present in the ionic state is given by the equation

$$[A'^*] = [A'_{\text{tot}}] - [AB]^* \quad (2)$$

where  $[AB]^*$  is the concentration of macroelement bound in the complex.

If the ratio of the stability constant of the microelement complex compound ( $\beta$ ) to that of the macroelement complex compound ( $\beta'$ ) is known along with the ratio  $[AB]^*/[A'^*]$ , it is then possible to find the concentration of the macroelement in the ionic state:

$$[A'^*] = \frac{[A'_{\text{tot}}]}{1 + \frac{\beta}{\beta'} \frac{[AB]^*}{[A'^*]}} \quad (3)$$

Substituting (2) and (3) into Eq. (1) and simplifying, we find

$$D_0 = \frac{x[A']_{\text{tot}}}{y[A']_{\text{tot}}} + \frac{x[AB]'}{y[A']} \frac{\left(\frac{\beta}{\beta'} - 1\right)}{\left\{1 + \frac{\beta}{\beta'} \frac{[AB]'}{[A']}\right\}}. \quad (4)$$

The first term of this equation is the experimentally determined cocrystallization coefficient  $D$ . Then, solving (4) for  $D$  and making use of (1), we obtain

$$D = D_0 \frac{\left\{\frac{[AB]'}{[A']} + 1\right\}}{\left\{\frac{\beta}{\beta'} \frac{[AB]'}{[A']} + 1\right\}}. \quad (5)$$

It is not difficult to show that under conditions such that  $[A'] \ll \frac{\beta}{\beta'} [AB]'$  and  $[A'] \ll [AB]'$ , Eq. (5) simplifies to  $D = D_0 \frac{\beta'}{\beta}$ , and the experimental crystallization coefficient assumes its limiting value.

The correctness of our Eq. (5) was confirmed for the distribution of  $\text{Sr}^{90}$  between the solution and the solid phase of barium nitrate. It was found that the cocrystallization coefficient at 25° for strontium in the absence of a complex former is  $D_0 = 0.13 \pm 0.01$ . When complexon III, which forms a stronger complex with strontium than with barium, was introduced into the system, the cocrystallization coefficient for strontium decreased. The results are shown in Table 1.

TABLE 1. Dependence of the Cocrystallization Coefficient for Strontium on the Extent to which Barium is Bound in the Complex

Expt. no.	$\frac{[AB]'}{[A']}$	$D$	$\frac{\beta}{\beta'}$
1	1.63	0.00648	31.8
2	0.456	0.0116	33.6
3	0.195	0.0235	28.7
4	0.0652	0.0509	26.4
5	0.0195	0.0829	30.7

Average 30.2

\*  $[AB]'/[A'] = [\text{Ba}]$  in complex /  $[\text{Ba}']$  in the ionic state.

this is that the coprecipitation experiments were carried out under conditions such that the ionic strength was high (sodium nitrate concentration of 500 g/liter), and the activity coefficients of the components were not taken into account.

Thus far we have considered the effect of complex formation by the components on separations carried out under equilibrium conditions. It is now known that with regard to the separation of elements equilibrium cocrystallization is less effective than is the nonequilibrium cocrystallization described by the equation of Doerner and Hoskins [7]. Cocrystallization in accordance with the Doerner - Hoskins equation takes place during slow crystallization of the solid phase when the surface of the growing crystal is constantly in thermodynamic equilibrium with the solution. This is expressed by the equation:

$$\frac{dx}{a-x} = \lambda_0 \frac{dy}{b-y},$$

where  $x$  and  $y$  are the amounts of microcomponent and macrocomponent in the solid phase,  $a$  and  $b$  are the total amounts of microcomponent and macrocomponent in the system;  $\lambda_0$  is the cocrystallization coefficient, and, as shown by Khlopin [5],  $\lambda_0 = D_0$ .

It is evident that the introduction of a complex former into the system requires replacement of  $\lambda_0$  by  $\lambda$ , and  $\lambda$  must equal  $D$ . Then, from Eq. (5) and (6) we obtain

It is apparent from the table that the experimentally determined cocrystallization coefficient decreases with an increase in the amount of barium bound in the complex. At the same time, the ratio of the stability constants for the strontium and barium complexes, which may be calculated by Eq. (5), remains constant, within the limits of experimental error, which confirms the applicability of Eq. (5).

Thus, knowing  $D_0$  and  $\beta/\beta'$ , it is possible to calculate the amount of complex former which must be introduced into the system in order to obtain the required completeness of separation of the components.

It should be noted that our value of  $\beta/\beta' = 30.2$  differs from the value reported in the literature [6], 7.44. The reason for

$$\frac{dx}{a-x} = \lambda_0 \frac{\left\{ \frac{[AB]'}{[A^{*'}]} + 1 \right\}}{\left\{ \frac{\beta}{\beta'} \frac{[AB]'}{[A^{*'}]} + 1 \right\}} \frac{dy}{b-y}. \quad (7)$$

There are two possible methods for the precipitation of the solid phase:

1. Complex former is introduced into the system in an amount such that only parts of the macroelement and microelement are bound as complexes. Then, when precipitation is carried out slowly, a certain amount of the macroelement originally present in the ionic state is converted to precipitate.

2. The macroelement and microelement are initially converted to complexes. Slow decomposition of the complexes is then carried out. This gradually converts the elements to ions, and, in the presence of an excess of precipitant, they form a solid phase. In this case, it is assumed that the concentration of macroelement in the ionic state does not change during the precipitation process.

In the first case, the variable will be  $[A^{*}]$ . Expressing  $[A^{*}]$  in terms of  $\underline{b}$ ,  $\underline{y}$ , and  $[AB]'$  and simplifying, we obtain

$$\frac{dx}{a-x} = \lambda_0 \frac{dy}{b + [AB]'\nu \left( \frac{\beta}{\beta'} - 1 \right) - y}, \quad (8)$$

where  $\underline{\nu}$  is the volume of the solution.

Integrating the left side of Eq. (8) from 0 to  $\underline{x}$  and the right side from 0 to  $\underline{y}$  yields

$$\ln \frac{a}{a-x} = \lambda_0 \ln \frac{b - [AB]'\nu + \frac{\beta}{\beta'} [AB]'\nu}{b - [AB]'\nu - y + \frac{\beta}{\beta'} [AB]'\nu}. \quad (9)$$

Since  $[A^{*}_{init}]\nu = \underline{b} - [AB]'\nu$ , and  $[A^{*}_{fin}]\nu = \underline{b} - [AB]'\nu - \underline{y}$ , Eq. (9) finally becomes:

$$\ln \frac{a}{a-x} = \lambda_0 \ln \frac{[A^{*}_{init}] + \frac{\beta}{\beta'} [AB]'}{[A^{*}_{fin}] + \frac{\beta}{\beta'} [AB]'} \quad (10)$$

It should be noted that under conditions such that  $\frac{\beta}{\beta'} [AB]' \ll [A^{*}_{fin}]$ , complex formation no longer has an effect, and Eq. (10) simply becomes the Doerner-Hoskins expression:

$$\ln \frac{a}{a-x} = \lambda_0 \ln \frac{[A^{*}_{init}]}{[A^{*}_{fin}]}. \quad (11)$$

In the second case, the variable will be  $[AB]'$ .

Then, expressing  $[A^{*}]$  (7) in terms of  $\underline{b}$ ,  $\underline{y}$ , and  $[A^{*}]$  and simplifying, we find

$$\frac{dx}{a-x} = \lambda_0 \frac{\beta'}{\beta} \frac{dy}{b - [A^{*}]\nu + \frac{\beta'}{\beta} [A^{*}]\nu - y}. \quad (12)$$

Integrating the left side of this equation from 0 to  $\underline{x}$  and the right side from 0 to  $\underline{y}$  leads to the solution

$$\ln \frac{a}{a-x} = \lambda_0 \frac{\beta'}{\beta} \ln \frac{b - [A^{*}]\nu + \frac{\beta'}{\beta} [A^{*}]\nu}{b - [A^{*}]\nu - y + \frac{\beta'}{\beta} [A^{*}]\nu}. \quad (13)$$



Since  $[AB]'_{\text{init}} v = \underline{b} - [A''] v$ , and  $[AB]'_{\text{fin}} v = \underline{b} - \underline{y} - [A''] v$ , Eq. (12) finally becomes:

$$\ln \frac{a}{a-x} = \lambda_0 \frac{\beta'}{\beta} \ln \frac{[AB]'_{\text{init}} + \frac{\beta'}{\beta} [A'']}{[AB]'_{\text{fin}} + \frac{\beta'}{\beta} [A'']} \quad (14)$$

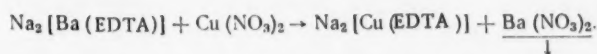
TABLE 2. Dependence of the Experimental CocrySTALLIZATION Coefficient on the Degree of Precipitation of Barium

Expt. no.	Degree of barium precip., in %	$\lambda$	Deviation from av
1	21,5	0,0030	-0,0002
2	32,7	0,0077	+0,0045
3	32,7	0,0049	+0,0017
4	43,1	0,0027	-0,0005
5	55,1	0,0022	-0,0010
6	64,6	0,0017	-0,0015
7	75,9	0,0016	-0,0016
8	86,2	0,0021	-0,0011
Average		0,0032	

A comparison of Eq. (10) and (14) shows that the second method of precipitation gives more effective separation of the elements.

Confirmation of Eq. (14) was obtained using the same system as in the preceding experiments.\*

A solution containing  $\text{Na}_2 [\text{Ba} (\text{EDTA})]$  and 500 g/liter of sodium nitrate was saturated with barium nitrate, and a trace amount of  $\text{Sr}^{90}$  was added. A solution of copper nitrate was then slowly added, with stirring, to a specific volume of the solution. The following reaction took place:



The barium displaced from the complex formed a solid nitrate phase. The rate of formation of precipitate was 0.1 g/hour. Upon completion of the experiment, the precipitate was separated, and the amount of strontium cocrySTALLIZED with the barium nitrate was determined. On the basis of the data obtained in these experiments, values of the experimental cocrySTALLIZATION coefficient,  $\lambda = \lambda_0 \frac{\beta'}{\beta}$  (see Table 2), were calculated by means of Eq. (14).

Examination of the table reveals that  $\lambda$  does not depend on the degree of barium precipitation. The value of  $\lambda = 0.0032 \pm 0.0015$  is close to the value calculated from the preceding data (cocrySTALLIZATION under equilibrium conditions):  $\lambda = 0.0043$ .

Thus, the experimental results confirm the correctness of the theoretical conclusions.

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\* A. B. Malinin and M. D. Nikonov assisted in this part of the work.

# THE INTERACTION OF BISMUTH CHLORIDE WITH ALKALI METAL CHLORIDES

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A number of investigations have been devoted to the behavior of bismuth in halide salt melts. Some of these were devoted to a determination of whether it is possible to purify metals by electrolysis [1, 2]. Others were devoted to the determination of bismuth electrode potentials [3-5]. Bismuth electrode potentials have been measured by various investigators using different reference electrodes, and are, therefore, not readily comparable. Moreover, the dependence of the equilibrium potential of the metal on temperature and concentration of metal ions in the melt has not been reported anywhere. Now a study of such a dependence would allow one to determine the nature of the interaction of bismuth ions with electrolytes of different compositions, in particular with anions and cations of the salt used as the solvent, and it would make possible correct organization of the electrolytic purification of bismuth.

The present work was devoted to a determination of the nature of the interaction of bismuth chloride with alkali metal chlorides over the temperature interval of 700 to 850°. With this aim, measurements of equilibrium potentials of metallic bismuth in electrolytes with different bismuth chloride contents were carried out. The experiments were conducted in the cell shown schematically in Fig. 1. It consisted of a quartz test tube installed in a steel block, which was heated by a furnace. The tube was completely closed by means of a rubber stopper.

An equimolar mixture of c.p. potassium and sodium chlorides, preliminarily purified by electrolysis, was charged to the test tube, and the alundum crucible was then placed in the tube. After fusion of the salt mixture, the metallic bismuth, which had priorly been purified by electrolysis, was introduced into the crucible. The bismuth chloride was prepared directly in the electrolyte by anodic solution of part of the bismuth metal in the crucible. The molybdenum cathode was placed in the electrolyte in the quartz test tube. Thus, the alundum crucible served here as a diaphragm separating the anolyte from the catholyte. The bismuth content of the melt was controlled by the amount of electricity passed through the electrolyte, and it was determined by chemical analysis of the crucible contents after the end of the experiment.

Fig. 1. Cell. 1) Quartz test tube; 2) chloride half cell; 3) small graphite tube; 4) electrolyte; 5) asbestos diaphragm; 6) molybdenum conductor; 7) thermocouple; 8) alundum crucible; 9) bismuth electrode.

In order to avoid the action of air on the salt melt, the air in the gas space in the cell was removed by evacuation, and the space was filled with purified helium. Measurement of the bismuth electrode potentials relative to a chlorine reference electrode [6, 7] were carried out by means of a PPTV-1 high-resistance potentiometer. The null indicator was a galvanometer with a sensitivity of  $10^{-9}$  amp per division. The temperature of the melt was maintained constant within the limits of  $\pm 3^\circ$  by means of a constant-voltage transformer, and was measured with a PPTV-1 high-resistance potentiometer in combination with a sensitive galvanometer.

In order to obtain reliable emf values, only those values which remained constant within  $\pm 1$  mv for not less than one hour were recorded.

The emf between the bismuth and chlorine electrodes in melts containing 1.13, 3.05, and 12.06 wt. % Bi was measured at different temperatures; these are shown in Fig. 2. It is evident that the cell emf decreases linearly with temperature. The experimental points plot quite satisfactorily as straight lines represented by the following empirical equations:

$$E_1 = 1,446 - 2,95 \cdot 10^{-4} T_v$$

$$E_2 = 1,412 - 2,90 \cdot 10^{-4} T_v$$

$$E_3 = 1,378 - 3,00 \cdot 10^{-4} T_v$$

Both the electrochemical potential difference, which was the subject of interest in this investigation, and the back thermal electromotive force between the molybdenum and carbon conductors entered into our measurements.

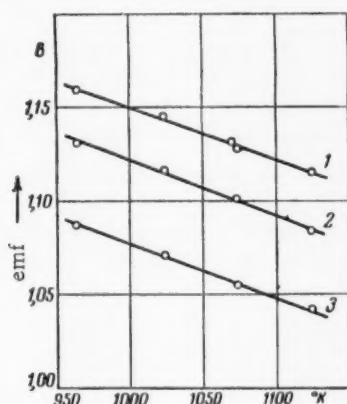


Fig. 2. Dependence of cell emf on temperature. Bi concentration in the melt: 1) 1.13 wt. %; 2) 3.05 wt. %; 3) 12.06 wt. %.

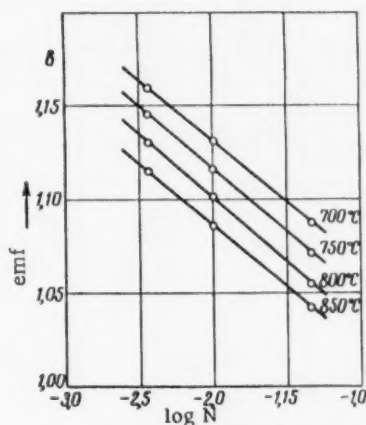


Fig. 3. Dependence of cell emf on bismuth chloride concentration,  $N$ , in the melt.

The temperature dependence of the thermal emf is given by the equation  $\varepsilon_T = 0.008 - 0.17 \cdot 10^{-4} T_B$  [8]. Taking into account the thermal emf between the graphite rod and the chloride electrode and between the molybdenum conductor and the bismuth, we obtain for the equilibrium potentials of bismuth relative to the chloride electrode in a molten equimolar salt mixture:

$$E_1 = -1,438 + 2,78 \cdot 10^{-4} T_v$$

$$E_2 = -1,404 + 2,73 \cdot 10^{-4} T_v$$

$$E_3 = -1,370 + 2,83 \cdot 10^{-4} T_v$$

Figure 3 presents the measurements in the form of isotherms showing how the cell emf varied with changes in the concentration of bismuth ions in the electrolyte. The experimental points fall on straight lines described by the following equations:

$$E_1 = 1,001 - 0,0650 \lg [\text{Bi}^{3+}] (700^\circ),$$

$$E_2 = 0,983 - 0,0665 \lg [\text{Bi}^{3+}] (750^\circ),$$

$$E_3 = 0,963 - 0,0695 \lg [\text{Bi}^{3+}] (800^\circ).$$

In these equations, the coefficients of the logarithmic terms expressing the bismuth ion concentration in the electrolyte are close to those of the logarithmic term in the thermodynamic equation for equilibrium electrode potential at the corresponding temperature:

$$E_{\text{Bi}/\text{Bi}^{3+}} = E_{\text{Bi}/\text{Bi}^{3+}}^0 + \frac{2,3RT}{3F} \lg [\text{Bi}^{3+}].$$

Consequently, the equilibrium potential of metallic bismuth relative to the chlorine reference electrode in the alkali metal chloride melt is described by the Nernst equation. This means that the liquid bismuth electrode is reversible with respect to  $\text{Bi}^{3+}$  ions in chloride melts, which behave as ideal solutions within the bismuth trichloride concentration range investigated. If it is assumed that the ideal behavior of these melts is retained over the entire range of  $\text{BiCl}_3$  concentration down to pure molten bismuth trichloride, then the emf of the cell



as calculated from our experimental data should be

$$E_e = 1,338 - 3,376 \cdot 10^{-4} T_v.$$

The temperature dependence of the emf of this cell as calculated from the literature data [9] can be represented as

$$E_r = 1,254 - 5,750 \cdot 10^{-4} T_v.$$

The difference  $E_e - E_r = 0,084 - 2,374 \cdot 10^{-4} T_v$  cannot be explained solely by errors in the measurements or by inaccuracies in the determinations of the thermodynamic values used in the calculation.

It is evident that this difference is due chiefly to the fact that the melts are not ideal solutions at high bismuth concentrations; i.e., a change in concentration is accompanied by rearrangements of the bismuth ions. The nature of these rearrangements can be judged by the difference  $E_e - E_r$ , found above. It apparently corresponds to a change in the Gibbs free energy during the transition from pure molten  $\text{BiCl}_3$  to a dilute solution of  $\text{BiCl}_3$  in a molten equimolar mixture of sodium and potassium chlorides, which behaves as an ideal solution:

$$\Delta F_{\text{mix}} = -3F(E_e - E_r) = (-5811 - 16,42T) \text{ cal/mole}.$$

It is apparent that when the salts are mixed there is a definite interaction accompanied by the liberation of heat ( $\Delta H_{\text{mix}} = 5,81 \text{ kcal}$ ) and by an increase in entropy ( $\Delta S_{\text{mix}} = 16,42 \text{ cal/degree/mole}$ ). The fact that heat is evolved when the salts are mixed indicates a strengthening of the bonds between the  $\text{Bi}^{3+}$  ions and the chloride anions with the formation of complex anionic groups.

Actually, the transition from pure molten bismuth trichloride to its dilute solution in the  $\text{KCl} - \text{NaCl}$  melt amounts essentially to substitution of alkali metal ions for part of the  $\text{Bi}^{3+}$  ions. Since the bismuth ions have three times the charge of the alkali metal ions, there is a change in the short-range order of the ions in the melt. The remaining  $\text{Bi}^{3+}$  ions more strongly hold the chlorine anions around themselves than do the alkali metal ions. In view of this, it is evident that bismuth is present in dilute solutions chiefly in the form of anionic complexes of the type  $\text{BiCl}_n^{(n-3)-}$ , where  $n > 3$ .

Complex formation by  $\text{Bi}^{3+}$  ions with chlorine anions has been studied in aqueous solutions by Noies, Holl, and Vitti [10]. On the basis of their data, Latimer [11] calculated the change in Gibbs free energy for the following process:



The change in Gibbs free energy for this process can also be calculated from our values for  $\Delta F_{\text{mix}}$  by extrapolation to a temperature of 298°K, taking into account the latent heat (2,6 kcal/mole) and entropy of fusion (5,2 cal/degree/mole) [11]:

$$\Delta F \text{ BiCl}_4^- = -3,21 - 11,22 \cdot 298 \cdot 10^{-3} = -6,56 \text{ kcal/mole}.$$

Such a close agreement of our value of  $\Delta F \text{ BiCl}_4^-$  with the value given in the Latimer monograph suggests that bismuth is present in alkali metal chloride melts in the form of anionic complex groups  $\text{BiCl}_4^-$ .

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# SYNTHESIS OF THE PARAAMINOSALICYLATE ESTER OF POLYVINYL ALCOHOL

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Over the past ten years, hundreds of new compounds have been synthesized and tested for tuberculosis therapy; however, it has been found that not one of them can replace streptomycin, phthivazide, and PASA with respect to therapeutic action [1]. Therefore, tuberculosis therapy remains basically a combination treatment in which streptomycin or phthivazide is used in combination with PASA.

PASA - paraaminosalicylic acid - is the first synthetic preparation to find widespread application in tuberculosis therapy. A fundamental disadvantage of it is its very rapid elimination from the sick organism [2]; 10 hours after administration, up to 60-80% of the PASA administered has been eliminated with the urine [3]. Therefore, in order to maintain a bacteriostatic concentration of PASA in the blood it is necessary to give the patient up to 15-20 g a day, which amounts to up to 1.5 to 2 kg during the course of medication [4]. It is natural that the introduction of such a

TABLE 1. Synthesis of the p-Aminosalicylate Ester of Polyvinyl Alcohol

Exptl. conds.	Moles chloride per 100 moles PVA	Reaction time, hrs.	Treatment	Presence of chlorine	Nitrogen content, %	Content of ester links		Qual. test for pres. of PASA (coupling with a diazo comp.)	PASA content, %	Intrinsic vis., $[\eta]^*$
						wt. %	mole %			
In pyridine medium, 100°	5	5	Reprecipitation with methanol	No	0.64	7.6	2.0	+	6.5	
	50	6	Reprecipitation with acetone	"	0.70	5.9	1.5		5.0	
In dimethyl formamide solution, 100°	20	5	Reprecipitation with methanol	"	0.36	12.2	3.3	+	10.4	0.4
	20	5	Reprecipitation with methanol	"	0.56	15.7	4.4		13.4	
	20	5	Reprecipitation with methanol	"	0.83	13.5	3.7		11.5	
	20	5	Reprecipitation with methanol	"	1.08	13.5	3.7		11.5	
	20	5	Reprecipitation with methanol	"	1.22	30.3	9.7		25.9	
	20	5	Reprecipitation with methanol	"	1.22	25	7.6		21.5	
	20	4	Extraction with pyridine	"	1.22	25	7.6		21.5	
	20	4	The same	"	0.96	10.8	3.0		9.25	
	20	4	The same	"	1.15					
	20	4	The same	"	1.20					
	20	3	" "	"	0.90					
	20	3	" "	"	1.20					
	20	3	" "	"	2.48					
	20	3	" "	"	2.24					
	20	3	" "	"	1.69					
	20	3	" "	"	2.12					
	20	3	" "	"	2.0					
	20	3	" "	"	1.86					
	20	3	" "	"	0.84					
	20	3	" "	"	0.86					

\* $[\eta]$  of the original polyvinyl alcohol was 0.44.

large amount of a chemical preparation into the sick organism causes numerous secondary reactions [5]. Therefore, the problem facing the chemists of the world is to change the PASA molecule so that there is a decreased rate of elimination of the preparation from the organism while retaining the therapeutic activity of the PASA [4].

In the present work, we undertook an attempt to modify the properties of PASA by means of a general method of modifying organic medicinal compounds by introducing the compound into the structure of the molecule of a synthetic polymer blood substitute so that the preparation can be administered by introduction into the blood stream (and also by subcutaneous and intramuscular injection). This method has previously been described by one of us [6]. The polymer used in the present work was polyvinyl alcohol.

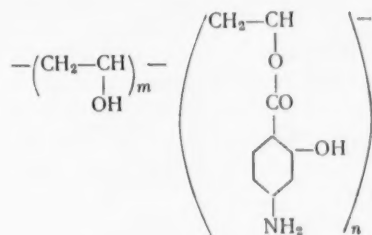
Since it is known that esterification of the carboxyl group does not decrease the therapeutic activity of PASA [7,8], we could assume that the *p*-aminosalicylate ester of polyvinyl alcohol would also exhibit bacteriostatic action against the tuberculosis mycobacterium.

The *p*-aminosalicylate ester of polyvinyl alcohol was prepared by esterification of polyvinyl alcohol with PASA chloride. The dihydrated sodium salt of *p*-aminosalicylic acid was used as the starting material. The *p*-aminosalicylic acid was precipitated from an aqueous solution of the sodium salt of PASA with hydrochloric acid at a pH of 3 [9, 10]. The *p*-aminosalicyloyl chloride was prepared by the action of thionyl chloride [11] on *p*-aminosalicylic acid in an ether medium or in solution in pyridine and subsequent precipitation with chloroform.

The resulting acid chloride contained as an impurity the product of the condensation of two molecules of PASA chloride by interaction of amino and chloro groups of neighboring molecules.

The esterification of polyvinyl alcohol with PASA chloride was carried out in a pyridine medium or in solution in dimethylformamide (see Table 1). When the synthesis was carried out in a pyridine medium, the method was that generally used for the preparation of esters of polyvinyl alcohol [12, 13]. A weighed amount of polyvinyl alcohol was swelled in pyridine at 30-40° for a period of 10-20 hours. It was then transferred to fresh pyridine, the acid chloride was added, and the reaction was carried out by stirring and heating to 100° over a period of 6 hours.

The reaction product was then washed with fresh pyridine, twice reprecipitated with acetone from aqueous solution, and washed with fresh acetone and ether. Water-soluble copolymers of vinyl alcohol with the *p*-aminosalicylate ester of vinyl alcohol were obtained; the content of ester links in these copolymers was 1-2 mole % (4-7 wt. %). The content of ester links was calculated from the nitrogen content of the samples, and the nitrogen content was determined by the micromethod of Dumas (under conditions such that chlorine was completely absent).



A significantly greater degree of esterification was obtained when the esterification was carried out in dimethylformamide solution (as recommended for the synthesis of cellulose esters [14]). A weighed amount of polyvinyl alcohol (PVA) was dissolved in dimethylformamide, the solution was heated to 130°, and a solution of PASA chloride (AC) in dimethylformamide was added. The reaction was carried out by stirring for 5 hours at 100°.

The resulting ester was precipitated with methanol from the reaction mixture, extracted with pyridine in a Soxhlet apparatus, and again precipitated from aqueous solution with methanol. The polymer was then washed with fresh portions of methanol and ether. A water-soluble product with a content of ester links of 3-10 mole % (10-30 wt. %) was obtained at a mole ratio of reactants of AC/PVA = 15/100 to 30/100.

In this way we have developed a fundamental method for the synthesis of this previously unknown derivative of polyvinyl alcohol.

Preliminary pharmacological tests carried out at the Leningrad Scientific-Research Institute for Tuberculosis and at Tuberculosis Clinic No. 8 by Doctor I. M. Rabinovich established that elimination from the animal (rabbits) of the

preparation prepared from low-viscosity (about 9 centipoises) polyvinyl alcohol took place several times more slowly than did the elimination of ordinary PASA preparation;\* specifically, PASA was detected in the organism over a period of 10-14 days. The residence time of the preparation in the organism can be increased still more by increasing the length of the polyvinyl alcohol paraaminosalicylic ester macromolecule.

When tested in vitro on Petraghani medium, it exhibited antimicrobial activity against the tuberculosis mycobacterium.

The properties of this preparation when used as a blood substitute in place of polyvinyl alcohol might be improved by using a copolymer of vinyl alcohol and vinylpyrrolidone.

The PASA-polyvinyl alcohol partial esters having a content of about 20 wt. % PASA vinyl alcohol ester were used for the preparation of thixotropic gels. These gels, with a melting point of 38-40°, were prepared by cooling 5-10% solutions of PASA polyvinyl ester to which had been added 2% boric acid or 3% congo dye. Such gels could be used for intramuscular or subcutaneous injections.

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\*PASAs were detected in urine by a colorimetric method using a 3% solution of  $\text{FeCl}_3$ .

# CIS-TRANS-ISOMERIZATION OF REPEATING UNITS OF 1,4-POLYBUTADIENE UNDER THE INFLUENCE OF NITROGEN DIOXIDE

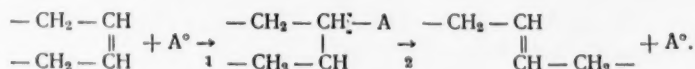
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for Synthetic Rubber

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The repeating units of natural rubber are known to undergo cis-trans-isomerization under the influence of various catalytic agents. Such an effect is produced by SO<sub>2</sub> [1-4], organoaluminum compounds, titanium halides [5, 6], anhydrous hydrogen chloride, etc. [6]. The possibility was also established of isomerization of cis repeating units of natural rubber at elevated temperatures under the influence of selenium [7], thioacids, and certain compounds that decompose by a radical mechanism, such as dibenzoyl disulfide [1-4]. It has been shown that 1,4-cis-polybutadiene can isomerize under the influence of ultraviolet rays and γ-radiation in presence of sensitizers [8, 9], and also under the influence of thioacids and some organic disulfides [1-4]. It has been suggested that isomerization is caused by consecutive reactions of addition of free radicals to the double bond and breakdown of the resulting products:



We have investigated the isomerization of cis-1,4-polybutadiene and of cis-2-butene (a hydrocarbon corresponding to the repeating unit of polybutadiene) in presence of nitrogen dioxide. Nitrogen dioxide is known as an active catalyst of cis-trans-transformation in a series of fatty acids and their esters [10-12].

We studied the isomerizing effect of nitrogen dioxide in 2% solutions of cis-1,4-polybutadiene and cis-2-butene in benzene. Experiments were run in partitioned glass ampoules. One compartment was filled with the calculated quantity of gaseous nitrogen dioxide and the other with a solution of the experimental substance. The sealed ampoule was thermostatted at the required temperature and the partition then broken with a lance. All experiments were performed in a medium of dry argon. At the end of an experiment the polymer was treated with alcohol and dried, while 2-butene was distilled off from the reaction mass. The molecular structure of the chain of each sample of polymer was determined, and the content of combined nitrogen also determined. The molecular structure of polybutadienes was investigated with the help of infrared absorption spectra. The content of 1,2- and trans-1,4 units was determined from the intensity of absorption at the maxima of the 909 and 967 cm<sup>-1</sup> bands. The change of cis-trans forms of butenes during the reaction was determined by chromatography.\* Nitrogen dioxide was prepared by thermal decomposition of pulverized and dried lead nitrate [13].

We showed that reaction of cis-1,4-polybutadiene with nitrogen dioxide leads to isomerization of the cis-units of the polymer chain to trans-units. In Fig. 1 are plotted the absorption bands of polybutadiene obtained after interaction with 6, 11.7, and 23.5 mole-% of nitrogen dioxide at a temperature of 96° for 2.5 hr.

Fig. 1 shows that the degree of isomerization increases with increasing NO<sub>2</sub> concentration; with 23.5 mole % nitrogen dioxide under these conditions a polymer containing about 60% of trans-units was obtained. Absorption bands

\* Z. D. Stepanova carried out the spectroscopic analyses of polybutadiene specimens; A. N. Genkin carried out the chromatographic analyses of mixtures of cis-trans-2-butenes.

for polybutadiene after treatment with  $\text{NO}_2$  at temperatures of  $-50^\circ$  and  $+96^\circ$  are plotted in Fig. 2. Isomerization does not take place at  $-50^\circ$ . Nitrogen dioxide is known to have a strong tendency to polymerize, and at temperatures below  $0^\circ$  it exists as the dimer  $\text{N}_2\text{O}_4$ . The concentration of the monomeric form increases with rising temperature, and the monomer is evidently responsible for the isomerizing action. In all the above experiments, both at  $+96^\circ$  and  $-50^\circ$ , nitrogen dioxide adds on quantitatively at the double bonds of the polymeric chain. The resulting products are insoluble in the hydrocarbon medium.

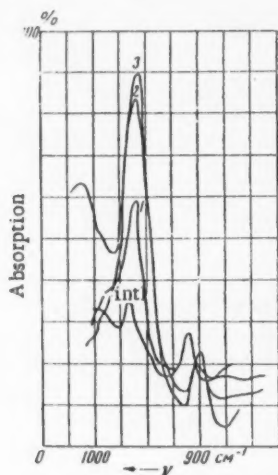


Fig. 1

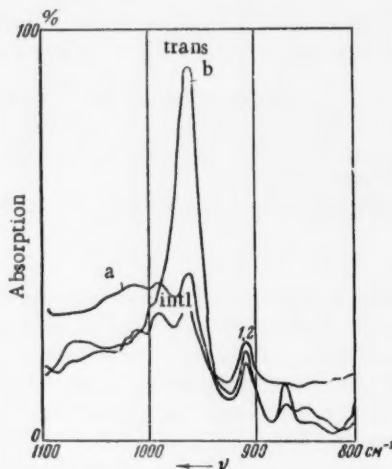


Fig. 2

Fig. 1. Infrared spectra of polybutadiene treated with  $\text{NO}_2$  at  $96^\circ$  for 2.5 hr: 1) 6 mole-%; 2) 11.7 mole-%; 3) 23.5 mole-%.

Fig. 2. Infrared spectra of polybutadiene treated with 23.5 mole % of  $\text{NO}_2$  for 2.5 hr: a) at  $-50^\circ$ ; b) at  $+96^\circ$ .

Similar results were obtained on reaction of  $\text{NO}_2$  with cis-2-butene. With a concentration of 6.0 mole %  $\text{NO}_2$  at  $90^\circ$  for 2.5 hr, 40% of the cis-2-butene was converted to trans-2-butene. It should be noted that the trans content in the polymer and in the butenes is not equal to the equilibrium content at  $90^\circ$ . This is apparently because the reaction does not proceed to the equilibrium state due to consumption of nitrogen dioxide in the addition reaction.

Our experiments have shown that hexaphenylethane at  $96$ – $130^\circ$  and diphenylpicryl hydrazide at  $20$  and  $60^\circ$  do not provoke any structural changes in the cis-1,4-polybutadiene chain. Disulfides (tetramethylthiuram disulfide, diisopropylxanthic disulfide, and mercaptobenzothiazole disulfide), which break down at  $120^\circ$  with formation of free radicals, lead only to gelation due to radical addition at the double bond without an isomerization effect.

It seems to us that the above-mentioned isomerization effects under the influence of  $\text{RS}^\cdot$  radicals are observed only when the main reaction is not radical addition at the double bond but cleavage of the H atom from the chain:



The mercaptan formed in step 1 participates in the chain transfer processes so that  $\text{RS}^\cdot$  radicals are regenerated. Such an isomerization must be accompanied by migration of the double bond.

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# INVESTIGATION OF THE INFRARED ABSORPTION SPECTRA DURING HARDENING OF RESOLIC PHENOL-FORMALDEHYDE RESIN

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and A. N. Shabalin

(Submitted by Academician V. A. Karegin, July 21, 1961)

Scientific Research Institute for Plastic Masses

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Considerable data have now been accumulated on the infrared absorption spectra of various types of phenol-formaldehyde resins. The infrared spectroscopic technique has nevertheless been very little employed for the study of the processes of setting of phenolic resins. The few publications in this field have not made a fresh contribution to existing ideas about the structure of hardened resins.

In the present paper we describe a study of the infrared absorption spectra of resolic phenol-formaldehyde resin during the process of setting at temperatures of 20 to 200°, using a more accurate spectroscopic technique (resin formed into disks with KBr). The investigated substance was a commercial resol resin which we prepared by the method described in more detail in [1]. After the resin had been dried in vacuo, it was subjected to molecular distillation at 80° and in a vacuum of the order of  $10^{-4}$  mm mercury. Specimens of hardened resin were prepared by compression in a heated cylindrical mold in the following manner: The initial resin was charged into the cold compression mold, a pressure of the order of 220 kg/cm<sup>2</sup> was applied, the heat was switched on, and the temperature of the mold raised at the rate of 1.5° per min until the desired level had been reached. This temperature was then maintained for 15 min. The mould was then quickly cooled to room temperature and the sample removed. The resulting cylindrical samples, diameter 10 mm and height 4-5 mm, were pulverized in a magnetic vibrating mill, mixed with KBr powder, and compacted in vacuo (10 tons/cm<sup>2</sup> [2]; the disk had a thickness of 1.45 mm and contained 6 mg of hardened resin. These disks were used for measurements of the absorption spectra of the hardened resin. Spectra were recorded with a two-beam Hilger H-800 spectrometer with a NaCl prism in the 700 to 4000 cm<sup>-1</sup> region.

The KBr disks used for taking the infrared spectra enabled accurate maintenance of the absorbing layer thickness so that the results were sufficiently reliable for conclusions to be drawn about the nature of the changes in the spectrum of the resin during setting. Evidence that the technique of preparation of the specimens for taking the infrared spectra (vibromill, use of high pressures for compacting of the disks, use of KBr as the medium) did not appreciably alter the spectra of the hardened resins was obtained by plotting the spectra of specimens of resin which had been hardened in a hot oven without pressure followed by vibratory grinding with KBr, and also of specimens of resin which had been compacted in admixture with KBr and hardened in the form of disks. The resulting spectra showed that the technique employed for specimen preparation does not influence the nature of the hardening process.

Using the above technique, we measured the infrared spectra of a resolic phenol-formaldehyde resin hardened at temperatures of 70, 130, 170, and 200°, also the spectrum of the initial unhardened resin. Our results are plotted in Fig. 1.

On the basis of several investigations [3] the bands observed in the spectrum of a resolic resin can probably be assigned as follows: The broad 3000-3600 cm<sup>-1</sup> band - valence vibrations of OH bonds; series of bands in the 2800-3000 cm<sup>-1</sup> region - valence vibrations of CH bonds; 1610, 1510, 1480 cm<sup>-1</sup> - planar vibrations of the benzene ring; 1450 cm<sup>-1</sup> - deformation vibrations of the CH bonds; 1370 cm<sup>-1</sup> - vibrations of the phenolic OH; 1225 cm<sup>-1</sup> - deformation vibrations of the OH bonds and valence vibrations of the C-O bonds; 1020 cm<sup>-1</sup> - deformation vibrations of the OH of the methylol groups; bands in the 750-900 cm<sup>-1</sup> region - non-planar deformation vibrations of the aromatic CH bonds characteristic of various types of substituted ring.

Judging by the data presented in Fig. 1, considerable changes occur in the spectra of the resin with increasing temperature of heating. Bands characteristic of the OH groups become smaller. This change can be associated with

the process of condensation (decreasing number of methylol groups). At the same time a broad band appears at  $1050\text{ cm}^{-1}$  which may be assigned to the valence vibration of the C-O ethereal bond. This would be consistent with the current theory that the methylol groups are at first converted into ethereal bridges. The  $1050\text{ cm}^{-1}$  band later decreased at  $150^\circ$  and completely disappears at  $170^\circ$ .

Particular interest is attached to the considerable diminution of the  $1370\text{ cm}^{-1}$  band which is characteristic of the vibrations of the phenolic OH groups. This diminution is observed already at relatively low temperatures ( $70^\circ$  and higher). Such a sharp drop in the band may be associated with the entry of the phenolic hydroxyl into reaction.

Yet another confirmation of the entry of the phenolic hydroxyl into reaction is the appearance in the spectrum of the hardened resolic resin (Fig. 1, d, e) of the  $1015\text{ cm}^{-1}$  band which is characteristic of aromatic ethers. Another new band developed in the spectrum is that at  $1645\text{ cm}^{-1}$  which is characteristic of C=C bonds. This band was earlier observed in the spectra of the hardened resin and was believed to be due to the formation of quinoid structures [4]. In this connection it is noteworthy that a double bond absorption band is already detected at  $130^\circ$  and then increases in size with rising hardening temperature. Comparison of the absorption spectra of hardened resins which were undistilled and those subjected to molecular distillation showed that the  $1645\text{ cm}^{-1}$  band is more prominent in the distilled resin.

The change in number and position of bands in the  $700\text{--}900\text{ cm}^{-1}$  region, characteristic of various substituted benzenes, is explained by processes of condensation of the resin which are accompanied by change in the number of substituents in the ring. This is reflected in the disappearance of the  $827\text{ cm}^{-1}$  band characteristic of the trisubstituted benzene ring, and in the development of two bands in the  $850\text{--}880\text{ cm}^{-1}$  region characteristic of tetrasubstituted benzenes. It is interesting that the  $1379\text{ cm}^{-1}$  band also makes its appearance in the spectrum of hardened resins. This can be attributed to formation of methyl groups. This band is very prominent at high hardening temperatures ( $170\text{--}200^\circ$ ).

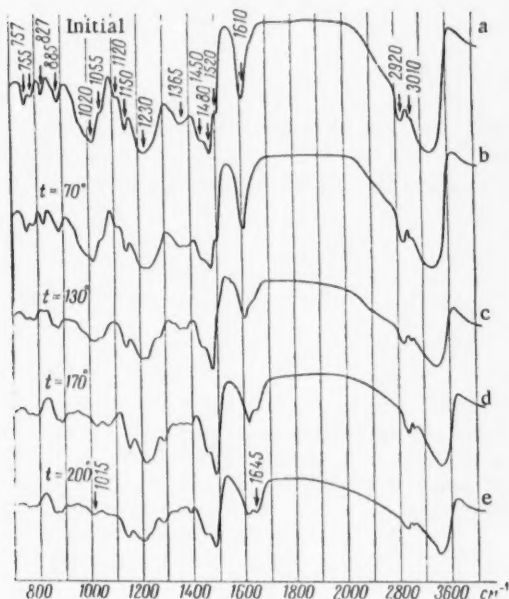


Fig. 1. Infrared absorption spectra of resolic resin hardened at various temperatures: a) initial unhardened resin; b)  $70^\circ$ ; c)  $130^\circ$ ; d)  $170^\circ$ ; e)  $200^\circ$ .

Our results do not easily permit any conclusions about the strengthening or weakening of hydrogen bonds during the setting of resolic resins. We can only say with certainty that the number of hydroxyl groups decreases, and in this connection the  $3200\text{--}3600\text{ cm}^{-1}$  band (corresponding to the valence vibrations of OH bonds) diminishes and its outline becomes sharper. Study of the infrared absorption spectra is, in our opinion, more rewarding if the spectroscopic data can be correlated with the change in other properties of the resins undergoing hardening — in particular their mechanical properties. A study of the change of mechanical properties of a resolic resin during hardening [1] led to the conclusion that an important part is played in the mechanism of hardening of resolic resins by formation of labile polymeric chains and their thermal breakdown, and by their recombination of the resulting active centers with formation of stable cross-linked structures. On the basis of the results of the present work, the theory may be advanced that the labile polymeric chains formed in the initial hardening stages of the specimen that we investigated are polyoxybenzyl ethers whose formation is the result of interaction between methylol groups. This conclusion is entirely consistent with the results of a series of investigations on model substances [5]. It is therefore extremely probable that breakdown of ethereal bridges is the source of the active centers whose recombination leads to a number of secondary reactions whose combined effect is the formation of stable, cross-linked structures — resites.

There are several theories about the mechanism of breakdown of ether bridges and about the nature of the resulting active centers. Particularly suggestive is the hypothesis [6] that breakdown of ether bridges leads to formation of quinomethides — extremely reactive compounds susceptible to further hardening reactions. As we saw above, the appearance of a double-bond absorption band, associated with quinomethides, was already observed by us at relatively low temperatures. Moreover the products of dimerization and trimerization of quinomethides are compounds of

low activity not susceptible to formation of polymeric chains. Also very improbable are "rearrangements" of the ether bridge, for example to a methylene bridge [7]. Such a mechanism would be difficult to reconcile with the observed effects of drastic thermal breakdown which lead to a sharp drop in mechanical strength of resolic resins at temperatures above 130°.

We put forward the hypothesis that a radical mechanism of ether bridge breakdown is extremely probable. In this event the intervention of the phenolic hydroxyl in the hardening reaction, as also the formation of a methyl group, can be explained in terms of recombination of the resulting free radicals. This hypothesis will be developed in more detail in a subsequent paper.

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# THE SIMPLEST UNSATURATED DIALKYLHYDRAZONES

B. V. Ioffe and K. N. Zelenin

(Submitted by Academician A. N. Nesmeyanov July 22, 1961)

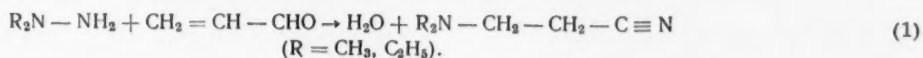
Leningrad A. A. Zhdanov State University

Translated from Doklady Akademii Nauk SSSR, Vol. 141, No. 6,

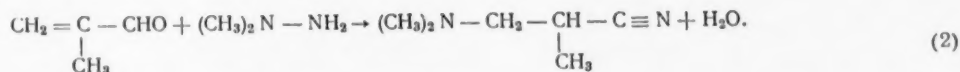
pp. 1369-1372, December, 1961

Original article submitted August 15, 1961

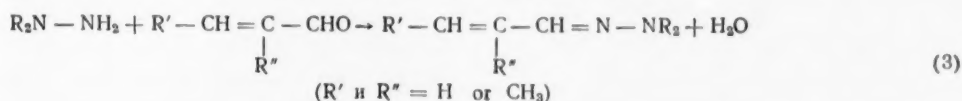
We showed earlier [1] that condensation of acrolein with unsymmetrical dialkylhydrazines in a weakly acid medium in the cold leads not to the expected unsaturated N,N-dialkylhydrazones but to  $\beta$ -dialkylaminopropionitriles:



It was of great interest to establish the field in which rearrangement was applicable. With this objective we have studied the reaction with dialkylhydrazines of the closest homologs of acrolein - crotonaldehyde and  $\alpha$ -methylacrolein. It was found that the "aminonitrile rearrangement" (1), which goes with facility with acrolein, was only observable in one case with the homologs under the same conditions, and then only as a secondary reaction.  $\beta$ -Dimethylaminoisobutyronitrile was isolated only in insignificant yield from the products of condensation of  $\alpha$ -methylacrolein with dimethylhydrazine:



The main products were the already known unsaturated N,N-dialkylhydrazones:



Under the same conditions, methyl vinyl ketone (the simplest unsaturated ketone) forms with diethylhydrazine, the normal product of reaction in accordance with (3), while with dimethylhydrazine it does not give the hydrazone but a water-soluble, high-molecular compound which was not further investigated. It should be mentioned that in all cases polymers were formed so that the yields were slightly lowered.

Characteristics of the unsaturated dialkylhydrazones, now synthesized by us for the first time, are set forth in Table 1.

Their structure was verified by hydrolysis in an acid medium to the original carbonyl compounds, and also by data for the characteristic frequencies in the infrared spectra.

The new unsaturated hydrazones are the simplest known compounds containing the C=C-C=N-N grouping. They are of considerable interest as examples of  $p$ - $\pi$ - $\pi$ -conjugated systems which have been studied very little. We see from Table 1 that the conjugated system C=C-CH=N-N (i.e. in hydrazones of aldehydes) is characterized by remarkably high exaltations of refraction and by great dispersion; these features have hitherto only been observed in systems with three conjugated multiple bonds ( $E_D$  3.3-3.4 and  $\omega_{FCD} \sim 51^\circ$  [2]).

An extremely interesting and specific feature of a conjugated system of this type is the wide variation in the effects of central disturbance of conjugation in dependence on the position of the side chain. In the case of compounds with central disturbance of conjugation at the C=C bond (hydrazones of  $\alpha$ -methylacrolein) we find the normal small depression of molar refraction and dispersion in comparison with unbranched isomers (hydrazones of crotonaldehyde). At the same time disturbance of conjugation at the C=N bond (in methyl vinyl ketone hydrazone) leads



TABLE 1.  $\alpha, \beta$ -Unsaturated N,N-Dialkylhydrazones

N,N-Dialkyl- hydrazone	Empirical formula	B.p., °C (pressure, mm)	$d_4^{20}$	$n_D^{20}$	$n_C^{20}$	$\Delta F_C^{20}$	MRD		Exaltation of refraction		$\omega_{FCD}$	C, %		H, %		N, %		Yield, %
							found	calc.	EMD	EED		found	calc.	found	calc.	found	calc.	
$\alpha$ -Methylacrolein dimethylhydrazone	$C_6H_{12}N_2$	56 (20)	0.8492	1.5051	1.4982	292.6	39.18	35.75	3.43	3.06	51.90	64.11	64.25	11.19	10.77	24.70	24.98	45**
$\alpha$ -Methylacrolein diethylhydrazone	$C_8H_{16}N_2$	67.8 - 68.5 (15)	0.8453	1.4951	1.4927	244.5	48.71	45.03	3.68	2.62	48.90	68.70	64.52	11.56	11.50	29.26	19.98	65
Crotonaldehyde dimethylhydrazone	$C_6H_{12}N_2$	70 - 71 (20)	0.8513	1.5152	1.5078	275.3	39.70	35.75	3.94	3.52	54.02	64.45	68.25	11.04	10.77	25.15	24.99	65
Crotonaldehyde diethylhydrazone	$C_8H_{16}N_2$	78.5 - 79.5 (15)	0.8503	1.5081	1.5013	251.0	49.17	45.03	4.14	2.95	49.40	68.97	68.52	11.73	11.50	19.77	19.98	73
Methyl vinyl ketone diethylhydrazone	$C_6H_{12}N_2$	46.3 - 46.8 (15)	0.8286	1.4614	1.4571	119.1	46.47	45.03	1.44	1.03	35.15	68.61	68.52	11.69	11.50	19.99	19.98	30

\* On the basis of the refractions of the Vogel bonds.

\*\* Yield and elemental analysis relate to 55-57° fractions (29 mm).

to unusually strong depression of refraction and dispersion. The depressions in the latter case are comparable with those for systems with two conjugated bonds, i.e. the effect of  $p-\pi$ -conjugation is substantially completely suppressed.

## EXPERIMENTAL

Before being brought into reaction, the initial substances were purified by distillation in a Vigreux column (15 plates). Aldehydes and methyl vinyl ketone were stabilized by a trace of hydroquinone.

$\alpha$ -Methylacrolein\* had the following constants after distillation: b.p. 68.0-68.2° (758 mm);  $d_4^{20}$  0.8389;  $n_D^{20}$  1.4154.

Crotonaldehyde was prepared by condensation of acetaldehyde [3]: b.p. 102.0-102.2° (763 mm);  $d_4^{20}$  0.8525;  $n_D^{20}$  1.4373.

Methyl vinyl ketone was synthesized by reaction of acetone with paraform [4]: b.p. 79.5-80.5° (760 mm);  $d_4^{20}$  0.8631;  $n_D^{20}$  1.4053.

The dimethylhydrazine and diethylhydrazine used were the same as in the preceding investigation [1].

## Reaction of dialkylhydrazines with carbonyl compounds.

To a solution of 78 g (0.5 mole) of  $NaH_2PO_4 \cdot 2H_2O$  (chem. pure) in 150 ml water was added 0.5 mole of dialkylhydrazine in the cold. To the resulting salt was added in the course of 15-20 min 0.5 mole of the carbonyl compound with continuous shaking and water cooling. After the lapse of 30 min the mixture was saturated with KOH; the organic layer was collected, dried over alkali, and distilled in vacuo in a 12-plate Vigreux column. In the case of methyl vinyl ketone the addition of alkali was accompanied by rapid darkening and resinification of the organic layer. No products other than a resin could be isolated in this case in the experiment with dimethylhydrazine. In all other experiments the main distillate fractions were products of normal condensation (3) - hydrazones.

$\alpha, \beta$ -Unsaturated N,N-dialkylhydrazones. These are yellow, oily liquids with a spicy odor, poorly soluble in water, which do not reduce Fehling solution at the boil. They are very weak monoacidic bases which titrate without a sharp change point in presence of bromophenol blue. The hydrazones are easily hydrolyzed to the original carbonyl compounds after brief boiling with 6 N aqueous solutions of inorganic acids. For the purpose of identification the products of hydrolysis were distilled into a solution of 2,4-dinitrophenylhydrazine or semicarbazide. The melting points of the derivatives obtained after hydrolysis agreed with those of the derivatives prepared from the original aldehydes and ketones (Table 2).

**Infrared spectra.** The instrument was a two-beam UR-10 automatic spectrophotometer, and the layer thickness 25  $\mu$  in the 700-4000  $cm^{-1}$  region. The spectra confirmed the structure of the hydrazones prepared.

\* We thank A. M. Kut'ina and M. A. Korshunov for kindly supplying the preparation.

Strong absorption bands were observed in all cases at 1570-1587  $\text{cm}^{-1}$ , and these must be assigned to the valence vibrations of the C=N bond in dialkylhydrazones (1575-1616  $\text{cm}^{-1}$  according to [6]). At the same time the spectra are lacking in the absorption bands of the C=O bonds (in the 1650-1750  $\text{cm}^{-1}$  region) and the C $\equiv$ N bonds (in the region of about 2250  $\text{cm}^{-1}$ ). Retention of the double carbon-carbon bonds and their unchanged position are confirmed by the presence of absorption bands of the C=C valence vibrations at 1622-1646  $\text{cm}^{-1}$ , in agreement with the 1621-1647  $\text{cm}^{-1}$  reported [7] for  $\alpha,\beta$ -unsaturated carbonyl compounds. Moreover, according to [7] the spectra of methacrylaldehyde hydrazones contain bands of the valence vibrations of terminal  $>\text{C}=\text{CH}_2$  groups at 3087-3088  $\text{cm}^{-1}$  (3077-3902  $\text{cm}^{-1}$  according to [7]) and of the corresponding deformation vibrations at 899-901  $\text{cm}^{-1}$  (885-895  $\text{cm}^{-1}$  according to [7]). Bonds of the C-H valence and deformation vibrations in the trans-CH=CH- grouping are detected in the case of hydrazones of crotonaldehyde at 3012-3021  $\text{cm}^{-1}$  and 973-974  $\text{cm}^{-1}$  (3010-3040  $\text{cm}^{-1}$  and 960-970  $\text{cm}^{-1}$ , respectively, according to [7]). The spectrum of methyl vinyl ketone diethylhydrazone contains two pairs of bands corresponding to the valence (3030 and 3092  $\text{cm}^{-1}$ ) and deformation (940 and 995  $\text{cm}^{-1}$ ) vibrations of the hydrogen atoms of the vinyl groups.

TABLE 2. Melting Points ( $^{\circ}\text{C}$ ) of Derivatives of Carbonyl Compounds Obtained by Hydrolysis of Dialkylhydrazones

Initial hydrazone	Derivative	Preparation investigated	Authentic preparation	Literature data [5]
$\alpha$ -Methylacrolein dimethylhydrazone	Semicarbazone	195-196	195-196	198
$\alpha$ -Methylacrolein diethylhydrazone	Semicarbazone	194-195	195-196	198
Crotonaldehyde dimethylhydrazone	2,4-Dinitrophenylhydrazone	188-189	188-189	190
Crotonaldehyde diethylhydrazone	2,4-Dinitrophenylhydrazone	186-188	188-189	190
Methyl vinyl ketone diethylhydrazone	Semicarbazone	138-240	139-142	141

(trans) bond at 3012-3021  $\text{cm}^{-1}$  and 973-974  $\text{cm}^{-1}$  (3010-3040  $\text{cm}^{-1}$  and 960-970  $\text{cm}^{-1}$  respectively according to [7]). The spectrum of methyl vinyl ketone diethylhydrazone contains two pairs of bands corresponding to the valence (3030 and 3092  $\text{cm}^{-1}$ ) and deformation (940 and 995  $\text{cm}^{-1}$ ) vibrations of the hydrogen atoms of the vinyl groups.

**$\beta$ -Dimethylaminoisobutyronitrile.** The aminonitriles boil higher than the unsaturated hydrazones isomeric with them, and their refractive indices are very much lower. They must therefore be sought in the distillate fractions coming after the hydrazone fractions. A small quantity of such a fraction was detected only in the case of condensation of  $\alpha$ -methylacrolein with dimethylhydrazine. After three distillations of 9 g of combined fractions from three successive experiments carried out under similar conditions, there was isolated 0.8 g of a colorless, mobile liquid with a faint amine odor; b.p. 78.0-78.5 $^{\circ}$  (30 mm);  $n_D^{20}$  1.4259. Literature data for  $\beta$ -dimethylaminoisobutyronitrile [8]: b.p. 55-56 $^{\circ}$  (6 mm);  $n_D^{25}$  1.4210.

Found %: N 24.70; 24.83  $\text{C}_6\text{H}_{12}\text{N}_2$ . Calculated %: N 24.98.

The substance titrates sharply with 0.1 N aqueous HCl. Found: E 117; 118.  $\text{C}_6\text{H}_{12}\text{N}_2$ . Calculated: E 112.2.

The infrared spectrum of the substance contained a strong band at 2247  $\text{cm}^{-1}$  characteristic of the nitrile group.

A white precipitate of hydrochloride came down when a dry stream of hydrogen chloride was passed through an ethereal solution of the substance. The hydrochloride melted at 169-171 $^{\circ}$  after recrystallization from a mixture of ethyl acetate and methanol. According to the literature the hydrochloride of  $\beta$ -dimethylaminoisobutyronitrile melts at 171-172 $^{\circ}$  [8].

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# ADDITION OF THIOUREA AND SELENOUREA TO UNSATURATED ELECTROPHILIC REAGENTS

E. G. Kataev and L. K. Barinova

(Presented by Academician B. A. Arbuzov July 22, 1961)

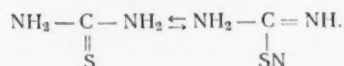
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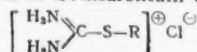
A study of the properties of thiourea showed that it gives two series of derivatives substituted at nitrogen and sulfur. This suggested the possibility of tautomeric equilibrium between the thiono and thiol forms:



Examination of the infrared and ultraviolet absorption spectra of thiourea [1], however, showed it to be the stable thiono form both in the crystalline state and in aqueous solutions, irrespective of the pH of the medium. All reactions of thiourea leading to formation of S-derivatives must therefore be regarded as a process taking place with transfer of the reaction center to the sulfur atom [2]. It is known that S-derivatives of thiourea are usually obtained by its reaction with halogen-substituted addends. Direct interaction of thiourea with unsaturated electrophilic systems

TABLE 1

Derivatives of Isothiuronium Chloride



Compound no.	R	Solvent	Yield, %	M.p., °C	Empirical formula	S, %	
						found*	calc.
I	-CH <sub>2</sub> -CH <sub>2</sub> -COOH	Alcohol, water	96,5	145	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> SN <sub>2</sub> Cl	—	—
II	-CH <sub>2</sub> -CH <sub>2</sub> -CN	Alcohol	93	161	C <sub>4</sub> H <sub>6</sub> N <sub>2</sub> SCl	19,51 19,29	19,33
III	-CH <sub>2</sub> -CH <sub>2</sub> -COOCH <sub>3</sub>	Alcohol	97,9	117	C <sub>6</sub> H <sub>11</sub> O <sub>2</sub> N <sub>2</sub> SCl	16,46	16,12
IV	-CH <sub>2</sub> -CH(COOH)-COOH	Acetic acid	86	168	C <sub>5</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> SCl	16,01 15,97	16,12
V	-CH <sub>2</sub> -CH(COOCH <sub>3</sub> )-COOH	Alcohol	80	156-157	C <sub>6</sub> H <sub>11</sub> O <sub>2</sub> N <sub>2</sub> SCl	15,51	15,63
VI	-CH(COOH)-CH <sub>2</sub> -COOH	Alcohol	82	200	C <sub>5</sub> H <sub>9</sub> O <sub>4</sub> N <sub>2</sub> SCl	13,84 13,72	14,00
VII	-CH=CH-COOH (trans)	Water	91,7	(decomp) 163	C <sub>4</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub> SCl	16,69	17,53

\* Analysis for sulfur was carried out by the method of N. V. Sokolova and V. A. Orestova [5], as improved at the Scientific Research Institute of the Rubber Industry.

is a neglected field of study since the scattered information in the literature about the ability of thiourea to enter into the cyanoethylation reaction has not been confirmed and challenged [3].

In 1951 Behringer and Zillikens [4] reported the interaction of thiourea with acrylic acid in presence of hydrogen chloride, but the authors did not discuss the reaction mechanism.

With the objective of a more detailed study of reactions of thiourea with unsaturated electrophilic reagents we carried out experiments on the addition of thiourea to acrylic acid (I), its nitrile (II), and methyl ester (III),

methacrylic acid (IV), methylmethacrylate (V), maleic and fumaric acids (VI), and citraconic acid, dimethyl maleate, and propiolic acid (VII) (see Table 1). It follows from the analytical data that all the adducts have a composition corresponding to addition of thiourea to the addends in the ratio of 1 : 1.

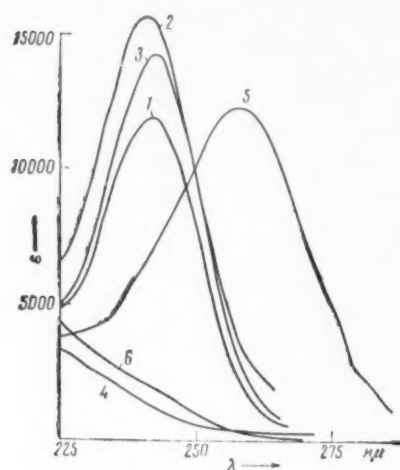


Fig. 1. Ultraviolet absorption spectra: 1) thiourea; 2) thiourea hydrochloride; 3) N-allylthiourea; 4) adducts of thiourea with acrylonitrile; 5) propiolic acid; 6) allyl chloride.

the absence of thiourea gave a negative result. The reverse process of isomerization of trans- to cis-acids is not observed, for fumaric acid normally reacts with thiourea to give an addition product.

The S-structure of the adducts was verified by data for the ultraviolet spectra of thiourea (1), thiourea hydrochloride (2), N-allylthiourea (3), and data for adducts of thiourea with acrylonitrile (4), propiolic acid (5), and allyl chloride (6) (see Fig. 1). On the basis of these data it was concluded that all the addition products that we prepared had S-structure. The absorption region of thiourea and N-allylthiourea has  $\lambda_{\max}$  242.5  $\mu$  ( $\epsilon_{\lambda_{\max}}^{(1)} = 11,900$  and  $\epsilon_{\lambda_{\max}}^{(3)} = 14,200$ ), whereas the spectra of adducts (4, 6) are lacking in absorption maxima in the 225-290  $\mu$  region that we studied. The strong absorption with shift of  $\lambda_{\max}$  in the 257.5  $\mu$  region for (5) must evidently be attributed to electronic transition due to the presence of a conjugated system in (VII). Definite interest is attached to the infrared spectrum of adduct (VII) (see Fig. 2) because it provides some evidence of the geometrical configuration of the double bond in adduct (VII). Occurrence of absorption in the 913  $\text{cm}^{-1}$  region (also in the 920  $\text{cm}^{-1}$  region for the adduct of selenourea with propiolic acid) points, in fact, to trans-configuration of adduct (VII),\* and consequently to a cis-mechanism of addition.

It was of interest to observe the geometrical isomerization of dimethyl maleate to dimethyl fumarate, of maleic acid to fumaric acid, and of citraconic into mesaconic acid during addition of thiourea. There are no grounds for attributing this phenomenon to the catalytic action of hydrogen chloride because a blank experiment in

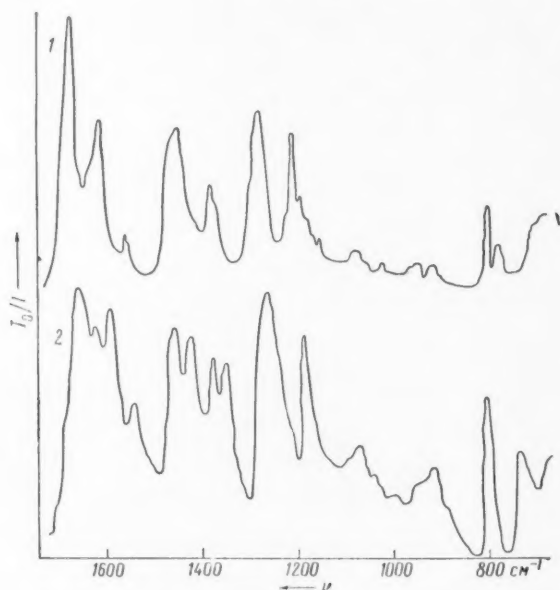


Fig. 2. Infrared absorption spectra of adducts with propiolic acid of thiourea (1) and selenourea (2).

\* The corresponding absorption band for the trans-ethylenic bond in  $\alpha$ -crotonic acid also lies in the 912  $\text{cm}^{-1}$  region [6].



Under similar conditions we studied the reaction (not previously studied) of selenourea with acrylic acid (VIII) and its nitrile (IX), also with propiolic acid (X). This reaction evidently proceeds by a similar mechanism (see Table 2).

In conclusion the authors extend thanks to É. G. Yarkova and R. M. Mamina for taking the infrared spectra.

#### EXPERIMENTAL

All the addition reactions were carried out in a medium of methanol or glacial acetic acid saturated with hydrogen chloride, or in 3.5 N aqueous hydrochloric acid solution. The duration of the reaction was 24 hr at room temperature. The addition products were isolated by concentration of the solutions in vacuo; they were then filtered and

TABLE 2  
Derivatives of Isoselenuronium Chloride

Compound no.	R	Solvent	Yield, %	M.p., °C	Empirical formula	Cl <sup>+</sup> , %	
						found	calc.
VIII	-CH <sub>2</sub> -CH <sub>2</sub> -COOH	Glacial acetic acid	65	151-152	C <sub>4</sub> H <sub>5</sub> O <sub>3</sub> SeN <sub>2</sub> Cl	15.23 15.26	15.32
IX	-CH <sub>2</sub> -CH <sub>2</sub> -CN	The same	51	167-168	C <sub>4</sub> H <sub>3</sub> SeN <sub>2</sub> Cl	16.56 16.54	16.60
X	-CH=CH-COOH (trans)	Water	94.4	184	C <sub>4</sub> H <sub>3</sub> O <sub>3</sub> SeN <sub>2</sub> Cl	15.53 15.57	15.46

recrystallized from methanol. All the adducts are stable to air and light. They are in the form of colorless, acicular crystals, soluble in water, ethyl alcohol, and (with heating) glacial acetic acid.

The infrared absorption spectra were taken with a two-beam Hilger H-800 spectrophotometer in the 700-2000 cm<sup>-1</sup> region with a sodium chloride prism. The compounds were introduced in the form of a thin suspension in paraffin oil.

The ultraviolet absorption spectra were measured in alcoholic solutions with the SF-4 spectrophotometer.

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# NEW DATA ON REDUCTION OF COPPER OXIDES BY GASEOUS REDUCING AGENTS AT LOW TEMPERATURES ( $< 100^\circ$ )

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(Presented by Academician A. N. Frumkin, October 9, 1961)

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In continuation [1] of our study of the reduction of oxides of metals at the lowest temperature at which reduction of copper oxides by gaseous reducing agents is still possible, we encountered a number of phenomena which can be considered of practical and theoretical interest. In the present work we subjected to reduction preparations of copper oxides ( $\text{CuO}$  and  $\text{Cu}_2\text{O}$ ), taken in the loose or pelleted form, using pure carbon monoxide as reducing agent in one case, and carbon monoxide in admixture with other gases in another case. The investigation was carried out at temperatures of  $45$  to  $105^\circ$  in a glass apparatus consisting of a reaction vessel with a capacity of  $100$  ml and a coil for

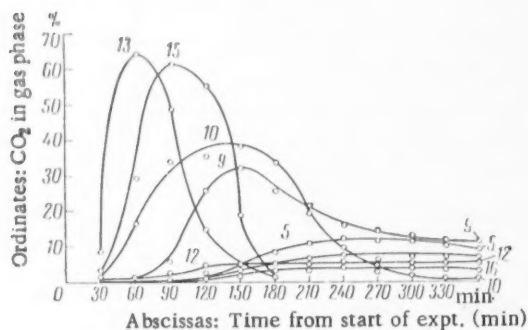


Fig. 1

subjected to x-ray analysis using  $\text{CuK}\alpha$  radiation and a Ni filter.

The experiments showed that when a sample was taken in loose form, a denser, brick-red core was formed at the start approximately at the center which with increasing degree of reduction increased in size. Even after complete reduction the surface of the sample was still covered with black spots. This contrast was especially conspicuous with a pelleted sample when the dark film covering the surface differed markedly in appearance from the brick-red interior of the mass. The latter, judging by the data of x-ray structural analysis, consisted solely of metallic phase. This shows that the reaction commences inside the sample and travels along a clearly defined front from the center of the sample to its periphery, so that the last part to be reduced is the film nearest to the fresh stream of carbon monoxide. This effect was observed in all experiments at below  $140^\circ$ ; only at higher temperatures did the red color of the reduced product make its appearance at the start of the experiment at the surface of the sample. In all cases the rate of reduction was greater with pelleted samples (see Fig. 1). This effect is particularly well illustrated by experiments at  $45^\circ$  when only pelleted  $\text{CuO}$  showed signs of reduction, as could be judged not only from the loss in weight of the sample but also by the formation of a thin brick-red band in the middle of the tablet. This phenomenon is also observed in experiments with  $\text{Cu}_2\text{O}$  in which reduction, if at all, only occurred in the compacted samples. The x-ray diagrams of residues obtained after short-period reduction of  $\text{CuO}$ , when much unreduced  $\text{CuO}$  still remained, never showed the presence of  $\text{Cu}_2\text{O}$  phase whereas reduced metal was very conspicuously indicated. Comparison of the kinetic curves of reduction of  $\text{CuO}$  at  $85$  and  $105^\circ$  reveals that the reaction rate is slightly higher at the lower temperature ( $85^\circ$ ), which suggests a non-linear relation between reaction rate and experimental temperature.

Experiments on reduction of oxides of copper with hydrogen at 85° (Table 2) showed unequivocally that under these conditions hydrogen has no reducing action at all on oxides of copper. Addition of 8% carbon dioxide to carbon monoxide greatly prolongs the induction period (Fig. 2), but once the reaction has commenced the CO<sub>2</sub> concentration in the gas phase can attain 75%.

TABLE 1

Sample no.	Substances	Type of sample	Temp., °C	Duration of expt. (min)	Weight loss (%)	Degree of reduction, %
1	CuO	Loose	45	360	none	none
2	CuO	Pellet	45	360	1,8	8,95
3	Cu <sub>2</sub> O	Loose	45	360	none	none
4	Cu <sub>2</sub> O	Pellet	45	360	none	none
5	CuO	Loose	65	360	5,08	25,28
6	CuO	Pellet	65	360	8,98	44,66
7	Cu <sub>2</sub> O	Loose	65	360	none	none
8	Cu <sub>2</sub> O	Pellet	65	360	none	none
9	CuO	Loose	85	360	17,56	87,33
10	CuO	Pellet	85	360	17,99	89,46
11	Cu <sub>2</sub> O	Loose	85	360	0,17	1,50
12	Cu <sub>2</sub> O	Pellet	85	360	5,60	46,16
13	CuO	»	85	180	17,96	89,32
14	Cu <sub>2</sub> O	»	85	180	1,40	12,52
15	CuO	»	105	180	17,87	88,87
16	Cu <sub>2</sub> O	»	105	180	1,30	11,63

\* The numbering of the samples corresponds to the numbering of the curves in Fig. 1.

Modern theory regards the reduction of metal oxides as adsorptive and autocatalytic processes [2-4]. No objection can be raised in principle to this approach, but it is too general and therefore does not fully explain the effects associated with reduction in individual cases. There are conflicting views [5], for example, about the reducing activity of hydrogen and carbon monoxide. Cases are known, however, when carbon monoxide reduces oxides with measurable velocity while hydrogen has no reducing action. Our data for the possibility of reduction of CuO directly to

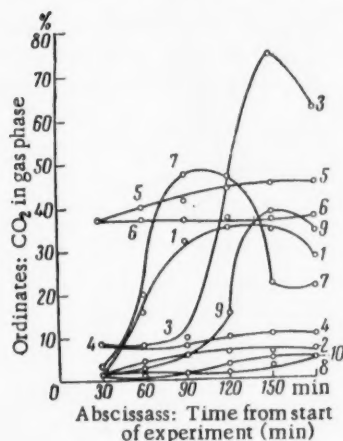


Fig. 2

The heterogeneous reaction of carbonyl formation proceeds wherever carbon monoxide is in contact with the surface of the original sample. Pelletting of the material cannot densify the powdered oxides of copper to such an extent that access of CO to the center of the sample is prevented, more especially since the system is put under high vacuum before the start of the experiment. At the start the activated adsorption of carbon monoxide therefore proceeds uniform-

metal without intermediate formation of Cu<sub>2</sub>O contradict the established view [6] of the inevitably stepwise character of CuO reduction. On the basis of existing ideas about the mechanism of reduction by gaseous reducing agents, it is difficult to explain why in our experiments samples which had been pelleted are more quickly reduced and why the process started in the middle of the sample and progressed from the center to the periphery. These effects may be explained by assuming that chemisorption of carbon monoxide on copper oxides involves the presence of metal ions as active centers with formation of a film of the type of M = C = O analogous in structure to metal carbonyls. Confirmation of the theory that reduction of copper oxides by carbon monoxide at temperatures at which thermal dissociation of the oxide is still impossible is associated with intermediate formation of carbonyl-like compounds is provided by the existence of an analogy between processes of reduction and synthesis and breakdown of metal carbonyls [7].

The following explanation of the reduction of copper oxides by carbon monoxide at temperatures below 110° may be advanced in the light of the foregoing discussion: The initial step is selective, activated adsorption when carbon monoxide molecules enter the crystal lattice and add on at the units of the expanded lattice, thus enabling formation of a carbonyl complex.

ly through the whole volume, which implies uniform carbonyl formation. But after formation of the carbonyl complex the latter is retained on the surface of the sample, and continuation of the process depends on desorption of the carbonyl to the gas phase or its breakdown and desorption of the decomposition products. Direct synthesis of carbonyl is accompanied by decomposition of the products which proceeds increasingly intensively with rising temperature. Pure carbon monoxide stabilizes the carbonyl complex and at the same time diffusion of CO to the middle of the sample proceeds with greater difficulty than to its surface; hence decomposition of the carbonyl complex at the center

TABLE 2

Sample no. **	Substance	Gases added	Weight loss, %	Degree of reduction, %
1	CuO	5% O <sub>2</sub>	15,40	46,58
2	Cu <sub>2</sub> O	5% O <sub>2</sub>	3,40	30,41
3	CuO	8% CO <sub>2</sub>	16,85	83,75
4	Cu <sub>2</sub> O	8% CO <sub>2</sub>	1,20	10,75
5	CuO	37% CO <sub>2</sub>	0,25	1,24
6	Cu <sub>2</sub> O	37% CO <sub>2</sub>	None	None
7	CuO	20% H <sub>2</sub>	16,77	83,40
8	Cu <sub>2</sub> O	20% H <sub>2</sub>	2,51	22,45
9	CuO	20% N <sub>2</sub>	13,67	67,98
10	Cu <sub>2</sub> O	20% N <sub>2</sub>	2,30	20,57
11	CuO	99% H <sub>2</sub>	None	None
12	CuO	99% H <sub>2</sub>	None	None

\* Duration of experiments 180 min; when using hydrogen, 360 min; heating temperature 85°; only pelleted samples were used.

\*\* The sample numbers correspond to the numbering of the curves in Fig. 2.

of the sample is more probable, and the reduction process starts from the internal parts of the sample. Reduction of copper oxides by carbon monoxide proceeds with considerable heat liberation, especially when CuO is reduced directly to metal. A sort of self-heating reaction takes place which is well illustrated by the kinetic curves. For the same reasons the reaction rate quickly falls when the reaction front has reached the peripheral portions. It is evident that densification (pelletting) of the substance creates the conditions in which zones with smaller heat dissipation are formed.

We see from the foregoing discussion that the highest rate of reduction is reached at 85° and not at the highest temperature of our experiments (105°). It may be suggested that this temperature creates the most favorable conditions for the individual steps of the process, in particular for the formation and decomposition of intermediate carbonyl-like compounds resulting from the chemical nature of the reducing agent.

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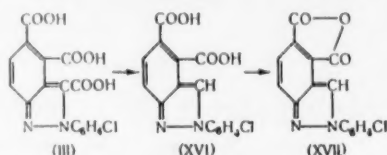
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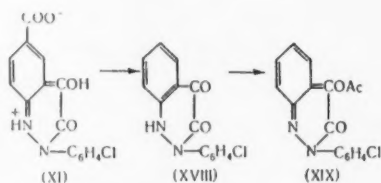
## 1299



Compound (III) is a tricarboxylic acid ( $C_{16}H_9O_6N_2Cl$ ) (titration with 0.01 N NaOH). On heating in glacial acetic acid for 2 hr it gives acid (XVI) and anhydride (XVII). Study of the infrared spectrum of compound (III) showed the presence of the carbonyl of a carboxylic acid ( $\nu$  1715  $cm^{-1}$ ) and of the C = N grouping ( $\nu$  1665  $cm^{-1}$ ), while the infrared spectrum of anhydride (XVII) contained two bands (1768  $cm^{-1}$  and 1842  $cm^{-1}$ ), characteristic of phthalic anhydride, and a band at 1636  $cm^{-1}$  evidently associated with the C = N group [2].



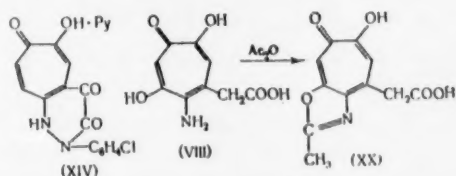
Compound (XI) ( $C_{15}H_9O_4N_2Cl$ ) has a yellow color, contains one carboxyl group, and possesses the properties of a betaine. These data are consistent with the infrared spectrum which contains a broad absorption band between 2020 and 3260  $cm^{-1}$ , resulting from internal interaction ( $COO^- \cdots NH$ ), and a band at 1559  $cm^{-1}$  characteristic of the C-O<sup>-</sup> group [2] and which we associate with the ionized carboxyl. The spectrum of compound (XI), on the other hand, contains an absorption band with the frequency of 1625  $cm^{-1}$  which is indicative of the presence of the C = N bond. Acid (XI) is decarboxylated on heating in pyridine or nitrobenzene to give compound (XVIII), which on heating in turn with acetic anhydride and  $H_2SO_4$  forms the acetyl derivative (XIX). Compound (XVIII) is amphoteric; it forms red salts with concentrated alkalis and yellow salts with concentrated inorganic acids. These salts probably have the o-quinoid structure of the type of (XIX). The structure of compound (XVIII) and of its derivative (XIX) was confirmed by their infrared spectra. The spectrum of the acetyl derivative (XIX) was found to contain the band of the carbonyl valence vibrations ( $\nu$  1749  $cm^{-1}$ ) characteristic of acylated vinyl alcohols [2], as well as an absorption band at 1613  $cm^{-1}$  which we associate with the C = N bond. In the infrared spectrum of (XVIII) was found the band of the NH valence vibrations ( $\nu$  3287  $cm^{-1}$ ).



Compound (XII) ( $C_{15}H_9O_4N_2Cl$ ) is obtained by the action of HCl on the pyridinium salt (XIV). It has a yellow color, possesses betaine properties, and gives a red coloration with  $FeCl_3$ . The betainic structure of this compound is confirmed by its infrared spectrum which contains a broad absorption band in the 2530  $cm^{-1}$  region associated with the presence of a bipolar ionic structure. Another band at 1558  $cm^{-1}$  is associated with the C-O<sup>-</sup> bond (similar bands are found in the spectrum of compound XI which is also a betaine). Further confirmation of the structure of compound (XII) is provided by the presence in its infrared spectrum of the band of the ketonic carbonyl valence vibrations ( $\nu$  1697  $cm^{-1}$ ), a band with the frequency of 1634  $cm^{-1}$  (associated with the C = N group), and a broad band in the 3160  $cm^{-1}$  region characteristic of hydroxyl with a strong intramolecular hydrogen bond. Concerning the pyridinium salt of this compound, the structure (XIV) follows from the fact that its infrared spectrum contains the band of the NH group valence vibrations ( $\nu$  3300  $cm^{-1}$ ) and also the ketonic carbonyl band ( $\nu$  1707  $cm^{-1}$ ).

The last of the substances that we isolated - compound (VIII) ( $C_9H_9O_5N$ ) - contains an enolic hydroxyl (blue coloration with  $FeCl_3$ ) and one carboxyl group (as found by titration with 0.01 N NaOH). This compound can undergo azo coupling with diazonium salts. However, it does not form diazonium salts, in which respect it resembles o-amino phenols which give diazo oxides. Distillation of compound (VIII) with zinc dust leads to formation of the pyrrole ring (identified in a qualitative test with a pinewood spill), while heating with acetic anhydride gives the oxazole derivative (XX). The tropolonic character of compound (VIII) and the nature of its substituents, as well as the structure of the oxazole derivative (XX), are supported by the infrared spectra. In the first case two bands were detected ( $\nu$  1609 and 3150  $cm^{-1}$ ), characteristic of the tropolone system [2], and also the valence vibration band of the OH group (in the vicinity of 3600  $cm^{-1}$ ), the NH group band ( $\nu$  3350  $cm^{-1}$ ), a band with frequency 1712  $cm^{-1}$  which was assigned to the carboxylic carbonyl. The oxazole derivative (XX) gave two bands ( $\nu$  1618 and 3150  $cm^{-1}$ ) which indicated the presence of the tropolone grouping, and the valence vibration band of the carboxylic carbonyl group ( $\nu$  1700  $cm^{-1}$ ).

The presence of the tropolonic system in compound (VIII) is indicated by the character of its ultraviolet absorption spectrum. The intensity of the main maxima ( $\lambda_{\text{max}}$  260 and 330 m $\mu$ , lg  $\epsilon$  4.34, and 3.87), like those of other tropolones, considerably exceeds the intensity of the same maxima in aromatic compounds of the benzene series [3, 4].



Taking into account the susceptibility of arylazotropolones to tautomeric transformation into tropoquinone hydrazones [1], we suggest that the compounds described above (III), (VII), (VIII), (XI), and (XII) are formed from azo compound (I) by a series of transformations of its tautomeric hydrazone form (IV) as set forth in Scheme 1. Compound (VIII), for example, might be formed by decarboxylation and rearrangement of tropoquinone hydrazone (IV) to *o*-troposemidine (V), which then hydrolyzes with detachment of *p*-chloroaniline to form the tropoquinoneimine (VI). This is reduced to the final tropolone (VIII) by the simultaneously formed reducing agents (II) and (IX). In this connection it should be noted that we earlier described [1] the susceptibility of tropoquinone hydrazone (IV) to decarboxylation, while its rearrangement to the troposemidine (V) is similar to the known transformation of 4-phenylazo-1-naphthol to 2-anilino-1,4-naphthoquinone [5].\* Concerning compound (III), it is evidently formed by aroma-

TABLE 1

Compound	M.p., °C	Solvent	Found, %				Calculated, %			
			C	H	N	Cl	C	H	N	Cl
(III)·H <sub>2</sub> O	259—261(decomp)	50% AcOH	50,74	2,92	7,38	9,81	50,74	2,93	7,40	9,36
(VIII)	297—298	MeOH	51,45	4,29	6,89	—	51,19	4,30	6,63	—
(XI)	277—278	50% EtOH	56,77	3,09	8,77	11,01	56,70	3,17	8,82	11,16
(XII)	257—258	—	56,24	3,25	—	—	56,70	3,17	—	—
(XIV)	261—262	Py	60,47	3,61	10,54	9,05	60,69	3,56	10,62	8,96
(XV)	285—286	Py	58,42	4,50	—	—	57,93	4,86	—	—
(XVI)·Py	264—265	Py	60,55	3,60	—	8,88	60,69	3,56	—	8,96
(XVII)	263—264	Glac. AcOH	60,24	2,43	—	11,62	60,31	2,36	—	11,87
(XVIII)	282—283	"	61,35	3,54	10,54	12,70	61,66	3,33	10,27	13,00
(XIX)	228—230	Dioxane	60,95	3,68	8,55	—	61,06	3,52	8,90	—
(XX)	237—238	EtOH	56,11	3,95	5,96	—	56,17	3,86	5,96	—

tization (usual for tropolones) of tropoquinone hydrazone (IV) to compound (II) which then undergoes dehydrocyclization under the influence of a strong oxidant — tropoquinoneimine (VI). The latter step is analogous to the previously known dehydrocyclization of azohinokitiol to hinopurpurin which is accompanied, as in the present case, by closure of the pyrazole ring [6]. Finally, compounds (XI) and (XII) probably originate with decarboxylation and hydration of tropoquinone hydrazone (IV), which leads to the hydrazo compound (IX). The latter undergoes oxidation by tropoquinoneimine (VI) to tropoquinone hydrazone (X), which then undergoes dehydrocyclization to (XIII). This compound is stabilized in the form of its inner salt (XII) or is aromatized to compound (XI). We earlier observed [1] this type of dehydrocyclization with other tropoquinone hydrazones of the type of (IV). It should be noted that the foregoing chain of oxido-reductive and hydrolytic transformations does not involve participation of oxygen of the air since identical results are obtained in the absence and presence of air as well as when the reaction is performed in a nitrogen atmosphere.

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\*It is interesting to note that the intermediately formed *o*-troposemidine (V) has the structure earlier assigned to hinopurpurin [7].

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# THE NEW SESQUITERPENIC HYDROCARBON DAUCENE

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V. L. Komarov Botanical Institute, Academy of Sciences of the USSR

(Presented by Academician B. A. Arbuzov, August 8, 1961)

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Original article submitted July 20, 1961

In studying the essential oil from the wild carrot *Daucus carota* L. we encountered a large variation in the composition of the oil depending on the place of origin of the carrot [1]. The essential oil isolated from the seeds of the wild carrot growing in Caucasia (Armenia) is composed mainly of carotol (80%). By repeated chromatographing of the sesquiterpene fraction of the oil on aluminum oxide (activity 1-2) we isolated the sesquiterpene bicyclic hydrocarbon daucene  $C_{15}H_{24}$  ( $\alpha_D + 23.32^\circ$ ), the properties of which are given in Table 1.

Exhaustive hydrogenation resulted in the absorption of 2 moles of hydrogen and the hydrocarbon of composition  $C_{15}H_{28}$  was obtained. The infrared spectrum (Fig. 1) of the hydrocarbon tetrahydrodaucene,  $[\alpha]_D + 2.40^\circ$ , is very close to the spectrum of daucane, obtained by Sorm [2], but also differs from it somewhat. Apparently, daucene has an azulenic structure; it contains two double bonds. The character of the double bonds follows from an analysis of the Raman spectrum. Two lines with  $\Delta\nu$  1669 (8)  $cm^{-1}$  and 1653  $cm^{-1}$  are found in the spectrum. The 1669  $cm^{-1}$  frequency corresponds to a secondary-tertiary double bond. As regards the line with  $\Delta\nu$  1653  $cm^{-1}$ , then it probably corresponds to the tertiary-tertiary double bond in the five-membered ring.

The infrared spectrum of daucene (Fig. 2) contains absorption bands in the vicinity of 1657  $cm^{-1}$  (slight intensity) and 829  $cm^{-1}$ . The latter band corresponds to the out-of-plane deformation vibration of =CH.

TABLE 1

	B.p. °C/mm	$d_4^{20}$	$n_D^{20}$	$[\alpha]_D$
Daucene	96°/4	0.8936	1.4918	+23.32°
Hydrocarbon from carotol	95-96°/5	0.8945	1.4903	+44.00°

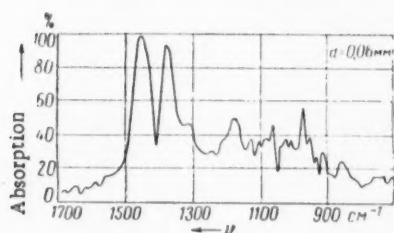


Fig. 1. Infrared spectrum of daucane

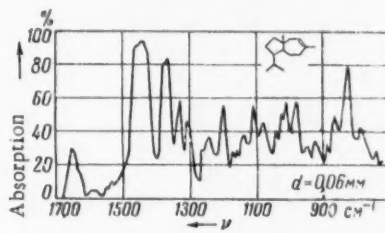


Fig. 2. Infrared spectrum of daucene.

It should be mentioned that when daucene is hydrogenated the first to disappear is the secondary-tertiary bond and the hydrocarbon  $C_{15}H_{26}$  ( $[\alpha]_D + 9.66^\circ$ ) is formed. The tertiary-tertiary double bond hydrogenates with considerably more difficulty. Daucene reacts with nitrosyl chloride to yield a nitrosochloride with m.p. 104°. The tertiary-tertiary double bond of the five-membered ring takes part in the formation of the nitrosochloride, since the absorption band in the vicinity of 1657  $cm^{-1}$  is absent in the infrared spectrum of the nitrosochloride.

The structure proposed by us for daucene follows from the fact that it is identical with the hydrocarbon obtained from carotol by dehydration in the presence of traces of sulfuric acid [3, 2].

The latter also forms a nitrosochloride (m.p. 107°) and has an identical infrared spectrum.

#### EXPERIMENTAL

The essential oil isolated from the wild carrot seeds had the following constants:  $d_4^{20}$  0.9272,  $n_D^{18}$  1.4978,  $[\alpha]_D^{23}$  +23.88°; acid number 0.22, ester value 20.0, OH content 5.80%, MR 66.31, calculated MR  $F_2$  66.14.

Found %: C 88.05, 88.22; H 11.8, 11.78  $C_{15}H_{24}$ . Calculated %: C 88.16; H 11.84

The spectrum of the Raman lines  $\Delta\nu$ : 257 (2), 296 (1), 369 (1), 385 (2), 431 (1), 506 (3), 595 (1), 635 (4), 658-683 (2), 846 (4), 887 (1), 948 (2), 977 (1), 1067-1169 (7), 1192 (6), 1306 (3), 1341 (3), 1375 (3), 1432-1463 (8), 1653 (8), 1669 (8), 2847-2966 (4).

Hydrogenation of daucene  $C_{15}H_{24}$ . The charge taken for hydrogenation was 6.08 g of the compound, 0.6 g of Pt (Adams) and 20 ml of glacial acetic acid. The amount of hydrogen absorbed was 688 ml (theory for one double bond = 662 ml). The isolated hydrocarbon had: b.p. 112°/17 mm,  $n_D^{20}$  1.4778,  $d_4^{20}$  0.8733,  $[\alpha]_D$  +9.66°.

Found %: C 87.27, 87.43; H 12.72, 12.75  $C_{15}H_{26}$ . Calculated %: C 87.29; H 12.71.

The spectrum of the Raman lines  $\Delta\nu$ : 345 (2), 640 (3), 841 (3), 1061-1103 (6), 1122-1158 (6), 1182 (6), 1343 (5), 1345 (1), 1397 (1), 1430-1461 (6).

Hydrogenation of dihydrodaucene  $C_{15}H_{26}$ . The charge was 1.8014 g of the compound, 0.2 g of Pt and 10 ml of glacial acetic acid. The hydrogenation required 20 hr. An additional 0.8 g of Pt was added during the hydrogenation. The amount of hydrogen absorbed was 187 ml (theory 198 mm). The isolated hydrocarbon  $C_{15}H_{28}$  had: b.p. 103°/5 mm;  $n_D^{20}$  1.4731;  $d_4^{20}$  0.8772;  $[\alpha]_D$  +2.40°.

Found %: C 86.61, 86.51; H 13.39, 13.42  $C_{15}H_{28}$ . Calculated %: C 86.45; H 13.54.

Analysis of daucene nitrosochloride with m.p. 104°:

Found %: C 66.56, 66.57; H 8.99, 9.11  $(C_{15}H_{24}NOCl)_2$ . Calculated %: C 66.80; H 8.90.

From the essential oil of the seeds of the wild carrot (*Daucus carota* L.), growing in Armenia, we isolated a new sesquiterpenic hydrocarbon of composition  $C_{15}H_{24}$  - daucene, belonging to the daucane type.

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## BORON COMPOUNDS.

### SYNTHESIS AND PROPERTIES OF TRI-( $\omega$ -STYRYL)-BORON

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and M. V. Kurashev

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Original article submitted October 2, 1961

In the present paper we describe the synthesis of tri-( $\omega$ -styryl)-boron, which was obtained by the reaction of the appropriate Grignard reagent [1] with boron trifluoride etherate. The ratio of Grignard reagent to boron trifluoride etherate plays an important role in the preparation of tri-( $\omega$ -styryl)-boron. Tri-( $\omega$ -styryl)-boron was obtained in about 76% yield in tetrahydrofuran medium, in a stream of dry argon, with the following molar ratio of the reactants:  $\text{Mg} : \text{C}_8\text{H}_7\text{Br} : (\text{C}_2\text{H}_5)_2\text{O} \cdot \text{BF}_3 = 7 : 3 : 2$ . The compound is obtained as slender needlelike crystals with m.p. 64-65°. Treatment of the reaction mixture with pyridine gave the complex  $(\omega\text{-C}_8\text{H}_7)_3\text{B} \cdot \text{C}_5\text{H}_5\text{N}$ , which was obtained as needlelike crystals with m.p. 138-140° (decompn.).

Attempts to synthesize tri-( $\omega$ -styryl)-boron using the same ratios of the reactants in a stream of pure nitrogen led to obtaining the complex  $[(\text{C}_6\text{H}_5\text{CH}=\text{CH}_2)_4]\text{MgBr}$ . This complex crystallizes from tetrahydrofuran solution with two molecules of the solvent, and from diethyl ether solution with three molecules of the solvent; the solvent is lost when the compound is heated, while at around 300° the complex decomposes with the formation of styrene and a carbonaceous deposit. The substance does not deliquesce in the air, but becomes coated with a white deposit. The crystals have m.p. 88-90° (decompn.). The complex reacts stormily with water to yield styrene, boric acid and  $\text{MgBrOH}$ . Treatment of the reaction mixture by the method described by V. A. Sazonova and N. Ya. Kronrod [2], followed by drying of the crystals, gave the anhydride of  $\omega$ -styrylboric acid.

Tri-( $\omega$ -styryl)-boron was isolated when the complex salt was treated with dry hydrogen chloride.

In the preparation of tri-( $\omega$ -styryl)-boron and its complex salt the experimental temperature was held at 40-45°. At higher temperatures the yield of the compound decreased sharply due to the formation of diphenylbutadiene as by-product.

Analogous results were obtained when the Grignard reagent was reacted with  $\text{BBr}_3$ .

The different results obtained when the experiments were run in a nitrogen or an argon atmosphere can be explained by the ability of argon to form coordination compounds with  $\text{BF}_3$  [3]. Apparently, argon forms an unstable coordination compound with the tri-(styryl)-boron, which dissociates completely into the components under the experimental conditions.

### EXPERIMENTAL

Tri-( $\omega$ -styryl)-boron. A mixture of 10 g of bromostyrene and 5.14 g of boron fluoride etherate was added to 3.3 g of magnesium turnings in 50 ml of tetrahydrofuran. The magnesium turnings were first activated by the addition of several drops of ethyl bromide. The reaction temperature during the entire experiment, and then for an additional 2 hr after the dropwise addition of the mixture had been concluded, was held within 40-45°. At the end of reaction the reaction mixture was filtered under argon pressure to remove the magnesium salts. The reaction mixture was then allowed to stand overnight and the tri-( $\omega$ -styryl)-boron deposited from solution as needlelike crystals. Yield 76%, m.p. 64-65°. The compound is soluble in benzene and tetrahydrofuran, and insoluble in chloroform and petroleum ether.

Found %: B 3.47; 3.48.  $(\text{C}_8\text{H}_7)_3\text{B}$ . Calculated %: B 3.38.

Complex  $(\text{C}_8\text{H}_7)_3\text{B} \cdot \text{C}_5\text{H}_5\text{N}$ . The filtrate from the removal of the magnesium salts, containing 3.4 g of tri-( $\omega$ -styryl)-boron, was treated with 0.83 g of pyridine in drops. Crystals of the complex deposited gradually from the solution, m.p. 138-140° (decompn.). The crystals are soluble in chloroform.

Found %: B 2.61; 2.58  $(C_8H_7)_3B \cdot C_5H_5N$ . Calculated %: B 2.71.

Anhydride of  $\omega$ -styrylboric acid. Previously cooled dilute acetic acid (1 : 10) was added to an ether solution of tri-( $\omega$ -styryl)-boron, obtained from 3.3 g of magnesium turnings, 10 g of bromostyrene and 5.14 g of boron fluoride etherate. The ether layer was separated, washed with water, and then washed three times with 2N NaOH. The combined alkaline extracts were washed with ether and then acidified with concentrated HCL solution. The precipitate was apparently styrylboric acid; however, when the crystals were filtered and then dried we obtained the anhydride of styrylboric acid with m.p. 151-152°. Yield 43%. The compound was obtained as colorless crystals, soluble in acetone and in alcohol.

Found %: B 8.15.  $C_{16}H_{14}B_2O_2$ . Calculated %: B 8.32.

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# EQUILIBRIUM OF THE TETRAZOLE AND AZIDE FORMS IN BENZOTHAIAZOLOTETRAZOLE

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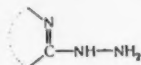
(Presented by Academician M. I. Kabachnik, July 18, 1961)

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Original article submitted July 17, 1961

The question of the structure of benzothiazolotetrazole has recently attracted the attention of a number of investigators [1-6].

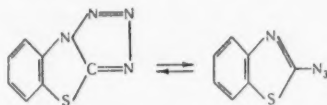
As is known, compounds obtained from the monohydrazines of N-heterocyclic compounds of structure:



and nitrous acid, or from the corresponding 2-chloro derivatives



and sodium azide, can be either tetrazoles or azides. Quite recently it was established that five-membered heterocycles, containing sulfur, occupy a unique position and give compounds that in the crystalline state are tetrazoles, and in solutions represent an equilibrium mixture of the two forms tetrazole  $\rightleftharpoons$  azide [4]. Thus, for benzothiazolotetrazole the following equilibrium exists in solutions:



Continuing our study of the hydrazines of benzazoles [7], and independent of the work of Boyer [4-6], we took the infrared spectra of benzothiazolotetrazole as crystals and in solution.\* The spectra of the solutions in different solvents displayed strong azide bands: a doublet of bands around 2155 and 2120  $\text{cm}^{-1}$ , which relate to the asymmetrical stretching vibration of the azide group, and a band in the 1255  $\text{cm}^{-1}$  region, corresponding to the symmetrical stretching vibration of this group [8]. In the crystalline state (mulls with vaseline oil and perfluorohydrocarbon) the substance fails to show any azide bands in the spectra but does exhibit bands that in the literature are usually attributed to the tetrazole ring (bands in the 1000-1100  $\text{cm}^{-1}$  and 760  $\text{cm}^{-1}$  regions) [9].

When the spectra of the compound in solution are compared with the spectra of the crystals (Fig. 1) it is easy to see that, depending on the nature of the solvent, the ratio of the azide and tetrazole forms proves to be different in solution. Thus, when dissolved in either benzene or carbon tetrachloride, benzothiazolotetrazole exists almost completely in the azide form (intense azide bands at 2155, 2120, and 1255  $\text{cm}^{-1}$  appear in the spectra, while the

\* A Zeiss UR-10 infrared spectrophotometer was used to take the spectra.

bands, observed in the crystalline compound and, consequently, characterizing the tetrazole structure, are absent). In dioxane and especially in pyridine solution, together with the bands characteristic for the azide form, the bands corresponding to the tetrazole structure are also present (1480, 1465, 1216, 760  $\text{cm}^{-1}$ ).

As a result, increasing the polarity of the solvent causes the equilibrium to shift in the direction of the tetrazole form.

When the spectra of pyridine and dioxane solutions of benzothiazolotetrazole were studied at different temperatures (in the interval 20-95°) we found that the intensity of the bands in the spectra depended strongly on the temperature, in which connection raising the temperature causes an increase in the intensity of all of the azide bands and a decrease in the intensity of the tetrazole bands. This indicates that the tetrazole-azide equilibrium is shifted

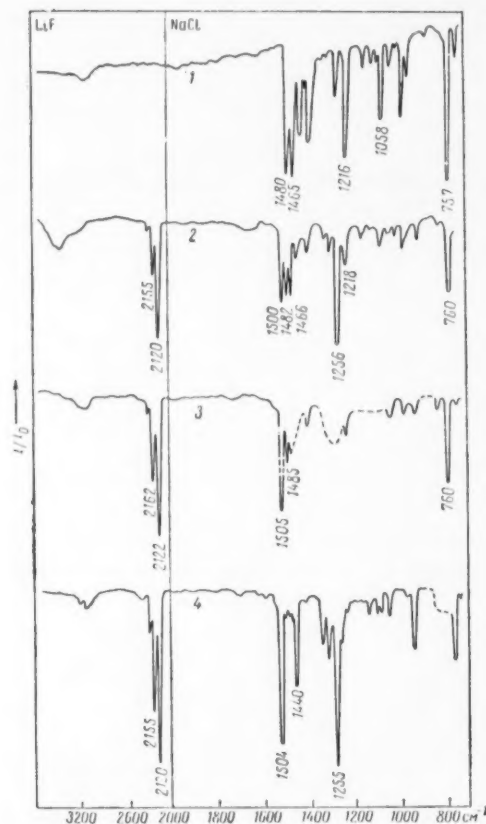


Fig. 1. Infrared spectra of benzothiazolotetrazole: 1) in the crystalline state (mulls with vaseline oil and polyfluorohydrocarbon); 2) in pyridine solution; 3) in dioxane solution; 4) in  $\text{CCl}_4$  solution.

The equilibrium tetrazole-azide is completely reversible, as is also the transition tetrazole to azide when in solution; after removal of the solvent the obtained crystals do not show any azide bands, strong azide bands appear when the crystals are redissolved, etc.

This type of opening and closing of the tetrazole ring on alternate solution and crystallization led us to postulate that an opening of the tetrazole ring and the establishing of equilibrium between the azide and tetrazole forms will also occur when the crystal lattice of the compound is destroyed on melting.

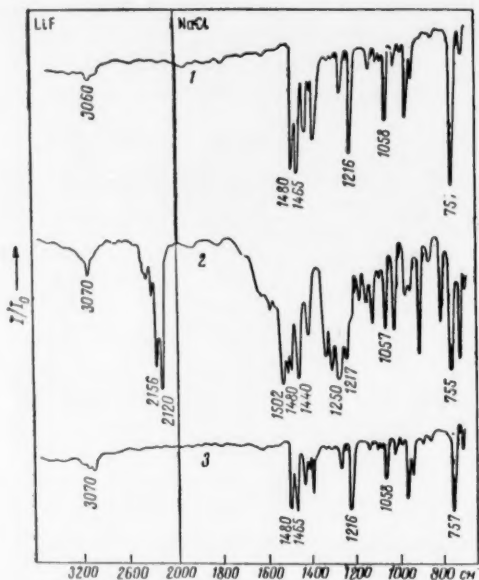


Fig. 2. Infrared spectra of benzothiazolotetrazole: 1) in the crystalline state; 2) in the molten state (at 120°); 3) in a crystalline film, formed after solidification of the melt.

toward the azide form when the temperature is raised. In  $\text{CCl}_4$  solutions a change in the intensity of the bands is not observed under these conditions, which is in agreement with the statement made above that in this solvent benzothiazolotetrazole exists almost completely in the azide form.

From the found temperature dependence we calculated the heat effect ( $-\Delta H$ ) of the transformation tetrazole-azide, which proved to be equal to 4650 cal/mole for the pyridine solution and 984 cal/mole for the dioxane solution.

Actually, the infrared spectra obtained by us of molten benzothiazolotetrazole (Fig. 2) at 115-120° exhibit very distinct bands of both the azide and the tetrazole forms, in which connection the amount of the latter is greater than in pyridine solution. Apparently, the polarity of the medium in the molten state is greater than in pyridine solution, and this is responsible for the further increase in the amount of the tetrazole form.

A disappearance of the azide bands is observed when the temperature of the melt is reduced to the point where it is completely crystalline, and the spectrum becomes identical with the spectrum of the starting crystals (Fig. 2). The process can be repeated several times, but either prolonged heating or a substantial increase in the temperature (above 120°) leads to an irreversible destruction of part of the compound, in which connection new bands appear, while the bands of the azide group do not disappear completely when the melt is cooled to the solid state.

As far as we know, the presented instance of equilibrium isomerism, consisting in the opening and closing of the tetrazole ring during alternate fusion and crystallization, has been observed for the first time.

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# REARRANGEMENT OF SOME ORGANOTIN AND -LEAD PEROXIDE COMPOUNDS

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(Presented by Academician M. I. Kabachnik, July 13, 1961)

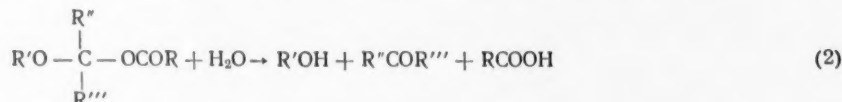
Translated from *Doklady Akademii Nauk SSSR*, Vol. 141, No. 6,  
pp. 1391-1394, December, 1961

Original article submitted July 12, 1961

A great interest in studying organometallic peroxide compounds has appeared recently. Methods of synthesis and the reactions of presently known organometallic peroxide compounds are discussed in detail in a recent review [1]. It is possible to assume that certain organometallic peroxide compounds are capable of undergoing rearrangements analogous to the perester rearrangements. As is known, Wieland and Maier observed the perester rearrangement of triphenylmethyl perbenzoate some thirty years ago [2]. Somewhat later, on the example of decahydronaphthyl perbenzoate [3], this type of rearrangement was studied and some rules pertaining to the course of such processes were established. Following this paper, a number of other authors [4-8] published their work on elucidating the mechanism of the rearrangement of various peresters. It was established that the mechanism of the rearrangement of peresters reduces to a migration of the alkyl or aryl group from the carbon atom, linked to the peroxide group, to the oxygen atom of the same group



Hydrolysis of the rearrangement product gives the alcohol, carbonyl compound, and acid



Several years ago this type of rearrangement was also observed for peroxide compounds of silicon, which in its chemical properties is a close analog of carbon. It was established that in the attempt to obtain trimethylsilicon perbenzoate from trimethylsilicon chloride and perbenzoic acid in the presence of ammonia a product devoid of peroxide oxygen was formed, which proved to be readily amenable to hydrolysis with the separation of benzoic acid. In the case of the analogous reaction using dimethylphenylsilicon chloride, the obtained compound on hydrolysis gave phenol, the yield of which was 66% of the theoretical [9]. Phenol was also found in the products of the reaction of dimethylphenylsilicon chloride with hydrogen peroxide in glacial acetic acid, in the presence of trace amounts of concentrated  $\text{H}_2\text{SO}_4$ .

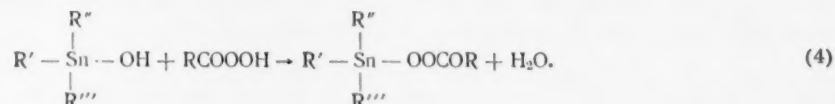
In both of these reactions it is possible to assume that the corresponding organosilicon peroxide compounds were formed, which, the same as in the case of peresters, underwent heterolytic rearrangement



Hydrolysis of the product from reaction (3) was accompanied by the formation of the compounds indicated above. In the literature it is indicated [10] that a rearrangement, analogous to the perester rearrangement, also exists

for the corresponding peroxide compounds of germanium. We made a study of the analogous rearrangement of organotin and -lead peroxide compounds.

As is known, the trialkyl- or triaryltin and -lead monohydroxides exhibit strongly defined basic properties. Consequently, such compounds should react with exclusive ease with peracids to yield the corresponding organometallic peroxide compound

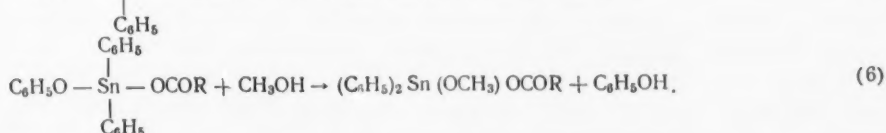
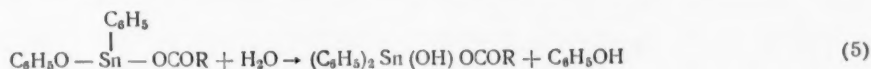


This organometallic peroxide compound should undergo rearrangement in accordance with reaction (1). Hydrolysis of the thus obtained rearrangement product should be accompanied by the separation of the corresponding organometallic oxides, as well as of other oxygen-containing compounds, which we actually observed. The homogeneous reaction mixture, obtained by mixing solutions of equimolar amounts of triphenyltin hydroxide and either peracetic or perpropionic acid in carefully dried methanol (initial concentration of the reactants in the solution was 0.2 mole/liter) at a temperature of 0°C, was allowed to stand in the dark at room temperature for 40-50 hr. The peroxide compounds present in the solution were completely consumed in this time, and handsome needle crystals gradually deposited from the solution. The evolution of gases was not observed in this reaction.

The precipitates that were separated from the solution and then carefully washed with methyl alcohol represented in the case of peracetic acid a material that did not melt up to 230°, while in the case of perpropionic acid the material softened at 170° and on further heating gave an infusible mixture of products, insoluble in cold benzene and difficultly soluble in hot benzene. On acid hydrolysis, the liberation of free acetic or propionic acid was shown in both cases. Based on the amount of liberated organic acid and the formation of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Sn(OH)Cl (m.p. 185°, from [11]; 187°) when the precipitates are heated with hydrochloric acid it is possible to conclude that the rearrangement of the corresponding organotin peroxide compounds, and their subsequent transformation, resulted in the deposition of crystalline reaction products, representing compounds of type (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Sn(OH)OCOR or (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnO · (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Sn(OCOR)<sub>2</sub>. Similar statements exist in the literature [11] for the alkyl derivatives of such organometallic compounds.

The yield of reaction product (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Sn(OH)OCOCH<sub>3</sub> or (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnO · (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Sn(OCOCH<sub>3</sub>)<sub>2</sub>, calculated on the basis of the starting triphenyltin hydroxide, was 72%. In the experiment with perpropionic acid the yield of the corresponding compound, isolated as precipitate, was 45%. However, alkaline hydrolysis of the compound, remaining in the alcohol solution, gave a substantial amount of finely crystalline substance, which had m.p. 128-130°, and proved to be soluble in methanol and insoluble in water. This substance was converted to (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Sn(OH)Cl when treated with hydrochloric acid.

In the case of both peracetic and perpropionic acid, after removal of the solid transformation products and unreacted triphenyltin hydroxide, phenol was isolated from the reaction mixture. This phenol was identified as tribromophenol (m.p. 95°, from alcohol), which did not depress the melting point when mixed with the authentic substance. The yield of phenol in the reaction with both peracids was 90% of theory, based on the starting hydroxide. The liberation of free phenol in the reaction mixture can be explained by the presence of the following reactions.



The reaction of triphenyllead hydroxide with peracetic acid in methyl alcohol, dioxane or ether was run in a similar manner.

When the reaction was run in methyl alcohol the homogeneous reaction mixture gave a negative test for peroxide oxygen after standing in the dark for 17 hr at room temperature and subsequent heating at 50° for 2.5 hr. During this time a small amount of gas, containing carbon dioxide, was evolved, and a small amount of diphenyltin oxide

was obtained as a precipitate. The oxide was identified by conversion to diphenyllead diacetate (m.p. 195-196°, mixed m.p. 198°). The precipitate was separated from the liquid reaction mixture by filtration. After treating the filtrate with aqueous caustic solution, followed by separation of the copious white precipitate, the phenol was isolated in the usual manner. The yield of the latter was 38%, based on the starting triphenyllead hydroxide. The above mentioned water-insoluble precipitate was separated using boiling methanol into triphenyllead hydroxide and diphenyllead oxide. The total amount of diphenyllead oxide isolated from the reaction mixture corresponded to 35% of the theoretical. The diphenyllead oxide was identified as diphenyllead diacetate, which was obtained by treating the diphenyllead oxide with acetic acid in boiling methanol.

The reaction of triphenyllead hydroxide with peracetic acid in dioxane went slowly because of the comparatively poor solubility of the starting organolead compound. However, also in this solvent, after long standing of the reaction mixture in the dark at room temperature and subsequent heating at 50° for 3 hr and at 70° for 1 hr, we isolated phenol from the reaction mixture, the amount of which represented 40% of theory, when based on the taken triphenyllead hydroxide. In this experiment, in the initial stage of reaction, a brief but quite noticeable evolution of gas was observed. Also, the peroxide compound present in the reaction mixture was not completely consumed during the entire time of observation.

When we attempted to react triphenyllead hydroxide with peracetic acid in diethyl ether we ran into difficulty, caused by the extremely low solubility of the starting organolead compound in this solvent. Still, even in this case, after shaking the heterogeneous mixture, composed of triphenyllead hydroxide, peracetic acid and diethyl ether, for 2 hr, a compound went into solution, which on hydrolysis liberated phenol. The yield of the latter was about 3%, when based on the starting lead hydroxide, which was only partially consumed in the reaction. In this experiment, the same as in the preceding experiment, a noticeable evolution of gas was observed at the very start of the reaction, but this soon diminished and then stopped completely.

Less definite results were obtained when we examined the reaction of triethyllead hydroxide with peracetic acid and with perbenzoic acid. When cooled to -10° ether solution of peracetic acid (initial concentration 0.33 mole/liter) was added to an equimolar amount of triethyllead hydroxide at the same temperature, the triethyllead hydroxide, very difficultly soluble in diethyl ether, quickly went into solution, which indicated the progress of rapid reaction between the reactants with the formation of the organolead peroxide compound. The rearrangement of this compound under the experimental conditions (-10°) went slowly, which was indicated by the slow decrease in the concentration of peroxide oxygen in the ether solution. Gas evolution was not observed in this case, but some coarse snow-white crystals deposited, which melted at 158° with decomposition. From the melting point of these crystals in the pure state and when mixed with pure triethyllead acetate (m.p. 160°), the isolated precipitate was identified by us as being triethyllead acetate. Its yield in the reaction mixture, which was allowed to stand in the dark for 36 hr at -10°, was 75%, when based on the starting triethyllead hydroxide.

The reaction of triethyllead hydroxide with peracetic acid in water solution (initial concentration of reactants 0.13 mole/liter) at room temperature went quite rapidly with very little gas evolution. The reaction mixture after standing in the dark at room temperature for a day gave a negative test for peroxide oxygen, but did give a qualitative test for acetaldehyde and tetraethyllead. The formation of the acetaldehyde can be explained by the easy oxidation by peracetic acid of the ethyl alcohol [12], liberated by a reaction analogous to reaction (5). The tetraethyllead can be formed as the result of the disproportionation of either triethyllead acetate or diethyllead diacetate, which were formed in the aqueous solution as the result of the main or secondary reactions [13].

The reaction of triethyllead hydroxide with perbenzoic acid in diethyl ether went in the same manner as in the above described reaction with peracetic acid. When the reaction with perbenzoic acid was run at the start for an hour at -20 to -10°, and then for 12 hr at room temperature, the presence of peroxide oxygen in the reaction mixture could not be detected. After this, triethyllead benzoate (m.p. 125-127°, the pure compound [14] has m.p. 127°) was isolated from the solution in a yield of 35%, based on the amount of triethyllead hydroxide taken for reaction. In addition to this compound, a very water-soluble organolead compound, which was not investigated closer, was also formed in the reaction. A water solution of this compound on long standing in the air gave a water-insoluble precipitate, which from the melting point (162°) was identified by us as being diethyllead dibenzoate, with m.p. 168° [14].

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# PREPARATION OF FLUOROPHENOLS BY THE HYDROLYSIS OF FLUOROHALOGENS

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We had previously shown that when fluorochlorobenzenes are reacted with aqueous ammonia in the presence of copper compounds only the chlorine atom is replaced by the amino group to yield the corresponding fluoroanilines and an explanation was given for this reaction course [1]. We assumed that a similar relationship will also exist in the case of replacing halogen atoms by the hydroxy group, i.e., when halobenzenes are hydrolyzed in the presence of copper compounds the ease with which the halogen is replaced should increase with increase in the atomic weight of the halogen. Consequently, it could be expected that in the catalytic hydrolysis of fluorohalobenzenes the main reaction products will be fluorophenols, and this would open up a new route to obtaining some interesting compounds.

As hydrolyzing agents we used weak bases-water solutions of the alkali metal fluorides and also potassium acetate, since it is known that hydrolysis with caustic alkalies can be accompanied by isomerization of the reaction products [2]. The hydrolysis of halo derivatives using metal fluoride solutions has not been reported before.

The experiments on the hydrolysis of the fluoro, chloro-, bromo- and iodobenzenes with aqueous potassium fluoride solution in the presence of cuprous oxide revealed that when heated at 250° for 4 hr the bromo- and iodobenzenes are converted almost quantitatively to phenol. The extent of chlorobenzene conversion under these conditions is slight, while fluorobenzene hardly reacts at all. Chlorobenzene is converted to phenol at a noticeable rate only at 300°. Hydrolysis of the fluorobromobenzenes gave the corresponding fluorophenols. The results of the experiments are given in Table 1.

TABLE 1

Expt. No.	Starting compound	Reaction products					m.p. of phen- oxyacetic acid
		name	yield, %	b. p., °C	m.p., °C	n <sub>D</sub> <sup>20</sup> (°) -	
1	<u>o</u> -Fluorobromobenzene	<u>o</u> -Fluorophenol	73	73/75 mm	—	1.5118 (22°)	139°
2	<u>m</u> -Fluorobromobenzene	<u>m</u> -Fluorophenol	78	177	—	1.5075 (21°)	115°
3	<u>p</u> -Fluorobromobenzene	<u>p</u> -Fluorophenol	73	179	47		104.5°
4	2,4-Difluorobromobenzene	2,4-Difluorophenol	53	150	20		126°

Replacing the potassium fluoride by an equivalent amount of either sodium or cesium fluoride, potassium bi-fluoride or potassium acetate is practically without effect on either the yield or the composition of the reaction products.

The secondary formation of from 1 to 3% of the corresponding fluorodiphenyl ethers occurs when the m- and p-fluorobromobenzenes are hydrolyzed. In the case of o-fluorobromobenzene about 2-3% of diphenylene dioxide is obtained. The formation of these compounds was proved by the identity of their infrared spectra and gas-liquid chromatograms with the authentic compounds. Acceleration of the reaction with increase in the atomic weight of the



halogen during catalytic hydrolysis makes it possible to state that the replacement of halogen by the hydroxy group in the presence of copper compounds, the same as the replacement of halogen by the amino group, proceeds through the intermediate formation of a complex of type  $\text{Ar}-\text{Hal}\cdot\text{Cu}^+$ , in which the copper cation is linked directly to the halogen atom [1].

By analogy with the noncatalytic amination of the fluorochlorobenzenes [3], we expected that also in the hydrolysis of the fluorohalobenzenes in the absence of copper compounds the fluorine atom will prove to be the more labile. Actually *m*-chlorophenol is formed when *m*-fluorochlorobenzene is heated with aqueous potassium acetate solution at 300° for 6 hr. Change in the order of halogen mobility when hydrolysis is in the absence of catalysts is explained by the fact that the reaction goes by the usual bimolecular mechanism of nucleophilic substitution.

#### EXPERIMENTAL

Into a rotated, 200-ml autoclave were charged 0.04 g-mole of halo derivative, 0.16 g-mole of sodium, potassium or cesium fluoride, potassium bifluoride or potassium acetate, 100 ml of water and 0.5 g of cuprous oxide. At the end of experiment the reaction mass was treated with 10 g of KOH and the unreacted starting product and diphenyl ethers were removed by steam-distillation. The residue from the steam-distillation was acidified, and the organic substances were extracted with ether (8 to 10 times with 50 ml portions), followed by drying over sodium sulfate. Then the ether was distilled off and the phenol was isolated from the residue by distillation. The properties of the phenols and of the phenoxyacetic acids prepared from them correspond to the literature data [4].

A mixture of 5.22 g (0.04 g-mole) of *m*-fluorochlorobenzene, 15.7 g (0.16 g-mole) of potassium acetate and 120 ml of water was heated for 6 hr at 300°. Using the above described procedure, we isolated 0.72 g of *m*-chlorophenol with b.p. 205-208°. The mixed melting point of the 2,4-dinitrophenyl derivative (m.p. 72°), prepared by the procedure given in [5], with the 2,4-dinitrophenyl derivative of authentic *m*-chlorophenol was not depressed.

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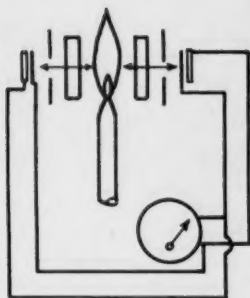
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Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	18	1959
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	Metalurg	Metallurgist	2	1957
Met. i top.	Metallogiya i topliva	Russian Metallurgy and Fuels	6	1958
Mikrobiol. OS	Mikrobiologiya Optika i spektroskopiya Pochvovedenie Priborostroenie	Microbiology Optics and Spectroscopy Soviet Soil Science Instrument Construction	26	1957
Pribory i tekhn. eksperimenta	Pribory i tekhnika eksperimenta	Instruments and Experimental Techniques	1	1959
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	1	1957
PTÉ	(see Priboi i tekhn. eks.) Problemy Severa	Problems of the North	1	1958
Radiotekh. i elektronika	Radiotekhnika i elektronika	Radio Engineering and Electronics	12	1957
	Stanki i instrument	Machines and Tooling	2	1957
	Stal'	Steel (in English)	1	1959
	Steklo i keramika	Glass and Ceramics	13	1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	4	1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primeneniye	Theory of Probability and Its Applications	1	1956
Tsvet. Metall	Tsvetnye metally	Nonferrous Metals	1	1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics - Uspekhi (partial translation)	66	1958
UKh	Uspekhi khimii	Russian Chemical Reviews	15	1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	1	1960
Usp. fiz. nauk	(see UFN)			
Usp. khim(ii)	(see UKh)			
Usp. matem. nauk	(see UMN)			
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Nonferrous Metals	1	1956
Vest. mashinostroeniya	Vestnik mashinostroeniya	Problems of Hematology and Blood Transfusion	48	1959
Vop. gem. i per. krov	Voprosy gematologii i pereivaniya krov	Russian Review of Biology	4	1959
Vop. onk.	Voprosy onkologii	Russian Engineering Journal	1	1957
Vop. virusol.	Voprosy virusologii	Problems of Hematology and Blood Transfusion	1	1957
Zavodsk. lab(oratoriya)	Zavodskaya laboratoriya	Problems of Oncology	1	1957
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Problems of Virology	1	1957
ZhETF	Zhurnal eksperimental'noi i teoreticheskoi fiziki	Industrial Laboratory Journal of Analytical Chemistry USSR	25	1959
Zh. eksperim. i teor. fiz.	Zhurnal fizicheskoi khimii	Soviet Physics-JETP	7	1952
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	28	1955
ZhMEI Zh(urn). mikrobiol. i epidemiol. i immunobiol.	Zhurnal mikrobiologii, epidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	7	1959
ZhNKh	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	1	1957
Zh(urn). neorgan(ich). khim(ii)			1	1959
ZhOKh	Zhurnal obshchei khimii	Journal of General Chemistry USSR	19	1949
Zh(urn). obshch(ei) khimii			23	1950
ZhPKh	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	1	1960
Zh(urn). prikl. khimii			26	1956
ZhSKh	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	1	1958
ZhTF	Zhurnal tekhnicheskoi fiziki	Soviet Physics-Technical Physics	1	1956
Zh(urn). tekhn. fiz.			1	1958
Zh(urn). vyssh. nervn. deyat. (im. P. Pavlova)	Zhurnal vysshei nervnoi deyatelnosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	1	1958



SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY  
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci. -Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci. -Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LEIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci. -Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci. - Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL -MES	Central Scientific Research Elec. Engr. Lab. - Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. -Publisher.



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by N. S. Poluéktov

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2,2'-Methylenedifuran  
N,N-Diethyl-2-Furamide  
5-Carboxy-2-Furanacetic Acid  
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Furan  
  
5-(Aminomethyl)-2-Furoic Acid  
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2-Furyl Methyl Ketone  
2-Benzylfuran  
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2,3-Dimethylfuran  
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Methyl 5-(Cyanomethyl)-2-Furoate  
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